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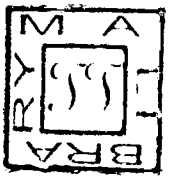
"PHYSICAL STUDIES ON THE STABILITY OF Cr (ii) and Co (ii), AND THEIR COMPLEXES"



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K.M. Abubacker.

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GENERAL INTRODUCTION

Problems related to the study of the oxidation states of elements and their stabilisation have attracted the attention of a large number of workers in the field of physical and inorganic chemistry. With improved experimental techniques, introduction of new and more reliable analytical and physical methods, and with the advancement in the ideas concerning the electronic arrangement of atoms and the quantum mechanical theories, our knowledge on the subject has considerably increased. As a result of this a large number of papers have appeared and are appearing in recent years both on the commonly known and less familiar oxidation states. To quote a few, these include the stabilisation of Cu(i and ii)[1-4], Ag(ii and iii)[5,3], Cr(0, i, iv and v)[7-11], Mn(0 and i)[12], Ni(0, i, iii and iv)[2,13], Co(0, i and v)[14,15,3], and cationic bromine and iodine[16] by co-ordination, and the formation of Mg(i)[17] and Al(i and ii)[18,19] by electro-chemical methods.

Inspite of the fact that considerable importance is attached these days to the preparation and characterisation of the less familiar oxidation states, some of the commonly known unstable valences still lack extensive and systematic study. In this connection attention may be drawn to two important compounds of the first transition series, namely, chromous chloride and potassium cobaltous cobalticyanide(ii). Both these compounds, besides being very unstable, present a number of interesting yet complicated features seldom met with in such other compounds. It appears

highly probable that some of the important aspects regarding their stabilisation remain unearthed till now and that there might lie further scope of work on this problem specially in view of the recent advancements in research techniques.

Chromous chloride is the first product of the reaction between chromium metal and hydrochloric acid, though it is never obtained by this method. The methods usually employed are: (i) by dissolving chromous acetate(obtained by reducing either chromic chloride or potassium dichromate) in hydrochloric acid and (ii) by the electrolytic reduction of chromic chloride. Of these the first method is used for the laboratory preparation of the compound. The solution obtained is deep blue in colour when kept properly stored out of contact with air. It invariably contains a little amount of chromic chloride and it is quite likely that the high degree of colour might be developed due to the association of two different states of oxidation in a single molecule(as in $CuCl_2$. CuCl, $Cs_2Au(i)Au(ii)Cl_6$). Besides the deep blue chromous chloride dark green, pale blue or light green or white isomerides have also been reported[20] while J.W. Mc Bain[21] obtained a dark green compound which gave a green solution with water changing to azure blue on keeping . Unlike chromic chloride[22] the different coloured varities are not said to be due to co-ordination with the water of crystallisation but due to partial hydration(loc. cit.) or due to the existence of various hydrates.[23] Although Cr(ii) compounds to some extent resemble Fe(ii) compounds, they are more strongly reducing so much so that chromous chloride is used for the quantitative

removal of oxygen from gas mixtures and as a useful analytical reagent for the quantitative estimation of a number of metal ions.[24,25] It has also been used in reducing organic compounds.[23] The behaviour of anhydrous chromous chloride with ether is interesting[27]. The solution obtained by extracting chromous chloride from a mixture of chromous and chromic loses almost all its reducing properties.

The readiness of chromous ions to get oxidised to Cr(iii) and their strong reducing properties necessitated the study of electrochemical measurements. Many workers carried out potential measurements of chromous-chromic system(vide infra) and data are available on the redox potential measurements with solutions prepared under different conditions and using a variety of electrodes. The earliest mention was made by Case[22] in 1823 who described a cell consisting of Sn and Pt electrodes in $CrCl_3$solution to have an e.m.f. 0 volt at ordinary temperature and 0.25 V. at 95°C(a value later on corrected to 0.44 V. at 15°C and 0.40 V. at 97°C by Skinner[28]). The best values obtained[30] were (chromic-chromous ratio 1:1, 18°C) e = 0.403 ± 0.003 V.in 0.02 M neutral acetate solution (using electrolytic Cr as electrode), e = 0.412 ± 0.002 V. in 0.003 N H_2SO_4; e= 0.454 ± 0.002 V. in weakly acid 0.4 M chloride solution and e = 0.398 ± 0.001 V. in 0.02 M chloride solution with Sn electrodes. All these measurements, however, suffered from [illegible] and were not carried out with a view to ascertain conditions in which analytical application of the system could be developed. This was first of all attempted

by Buhrer and Schupp[31] in 1926 and later on by Zintl and Rinacker[32] in 1927. The latter workers titrated directly copper sulphate with chromous chloride in acetic acid medium and recommended a temperature of 90°C and the presence of sufficient chloride ions for satisfactory results. Polarographic studies on the reduction of chromic chloride were taken up by M. Demassieux and J.Heyrovsky[33] in 1929 and they got breaks in the curves at 0.7 V and at 1.3 V, for the two stages Cr(ii) and Cr respectively. Further work on these lines was carried out by a number of workers with different isomeric forms of chromic chloride.

Although chromic ions have got the enormous power of forming complexes, the chromous ions form very few complexes and amongst them one or two are really stable. Descamps(1882)[34] prepared the unstable chromocyanide $K_4(CrCy_6)$ and stabilisation studies were carried out by Hume and Stone[35] in 1941. Of the various ammines the only stable one is $CrCl_2.6NH_3$[36]. Pyridine[37] and dipyridyl[38] complexes are unstable and oxidised by air. The double fluorides $KCrF_3$ and $NH_4CrF_3.2H_2O$[37] are also known but these too are unstable in solution. The only condition under which true stabilisation has been arrived at is by using hydrazine[37] as the complexing agent. This compound is not oxidised even when suspended in water and stirred with air ,The stability seems to depend on two factors: (i) using a solvent possessing reducing properties and (ii) insolubility in water. In recent years Lingane and Peesock[39] have drawn the attention towards the tendency for complex formation of $CrCl_2$ while studying the polarographic behaviour of Cr(ii) in various supporting electrolytes.

Potassium cyanocobaltate(ii) is obtained by adding a cold solution of potassium cyanide to cobalt chloride. The brown cobalt cyanide thus obtained is dissolved in KCN(at $0^{o}C$) which on addition of alcohol gives amethyst coloured crystals. Manchot and Herzog[40] studied its properties and found it to be quite unstable in solution at ordinary temperature, changing to cobalticyanide with the evolution of hydrogen. The solution, however, when prepared in KCN medium was found to be somewhat stable. In view of the ease with which it can pass over to the higher oxidation state, the compound is expected to act as a powerful reducing agent; but inspite of this it has found limited applicability as an analytical reagent due to its unstable nature and its tendency to form metal complexes. Redox potential measurements were taken up by Grube[41] in alkaline solution and there exists a controversy regarding the validity of his results[42]. Some work on the redox potential measurements have also been carried out in these laboratories and it seems difficult to achieve reversible and reproduceable results at the electrodes even in the presence of bases and neutral salts.

Another intresting aspect in the study of potassium cyanocobaltate(ii) is the controversy regarding its molecular formula and structure. Mondaine Monvail and Paris[43] on the basis of thermometric titrations gave the formula as $K_3Co(CN)_5$ while Szego and Postinelli[44] with the help of magnetic measurements reported as $K_4Co(CN)_6$. In recent years a number of workers, amongst whom Hume and Kolthoff,[41] Addison,[45] and Smith[46] may be mentioned, carried out polarographic radiochemical and potentiometric

studies with a view to establish its constitution. The problem of the structure, however, still attracts the fancy of research workers even when unanimity of opinion exists regarding its chemical formula.

The present piece of work deals with my studies on the stability of Cr(ii) and (anionic) Co(ii) and their complexes. The problem of stabilisation of the bivalent states of these two metals has been investigated in terms of the changes in the oxidation reduction potentials of chromous-chromic and cobalto-cobalticyanide systems and by preparing an insoluble complex which permitted the examination of the compound (containing Cr(ii) ions) both in the dry and the wet states. Keeping in view the work already done, investigations were carried out under the following plan :

Part 1. This part deals with the redox potential studies of chromous chloride solution(obtained by the reduction of chromic chloride with Zn and HCl) under different conditions, viz. using different electrodes, at different dilutions, and in presence of acids and neutral salts. It also includes the study of cathodic and anodic waves of Cr(iii) and Cr(ii) with a view to confirm the results on the potentiometric studies. The Cr(ii) ions have been stabilised by preparing the ferrocyanogen complex and its composition determined by chemical analysis, potentiometry, conductometry and amperometry.

Part 2. deals with analytical, redox potential and polarographic studies of potassium cobaltocyanide with a view to get some insight into the stability and structural aspect of the complex.

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CHAPTER - 1

Preparation, standardisation and properties of chromous chloride solution.

Chromous solutions (chloride or sulphate) can be prepared by a number of methods starting from chromic chloride or potassium dichromate. Different reducing agents like zinc and hydrochloric acid[1,2], amalgamated zinc[3-6] or lead[7], hydrogen peroxide[4], aluminium turnings[8] etc . have been used by different workers to obtain chromous chloride either in the form of hydrated crystals or in solution. In the anhydrous state it is obtained by the reduction of chromic chloride in a current of hydrogen[9,10], in the vapours of ammonium chloride or by passing hydrogen chloride over metallic chromium[11], at high temperatures.

Electrolytic reduction methods[12-16], have also been used from very early times for the preparation of chromous solutions, but these methods failed to give solutions containing Cr(ii) in a sufficiently large proportion.

Since the behaviour and stability of the chromous solutions are likely to vary from sample to sample depending on the mode of preparation, the amount of acid present, the extent of dilution and the method of storage, a specific method had to be adopted for the preparation and storage of chromous chloride solution for these investigations. The method recommended by Balthis and Bailar[2] with a slight modification was followed. chromic chloride was reduced with zinc and hydrochloric acid and the chromous chloride thus obtained was converted to

chromous acetate. The acetate was then decomposed by hydrochloric acid to get the chloride.

Preparation of the solution:-

The apparatus shown in the figure 1 was assembled. Sixty gms. of A.R. hydrated chromic chloride was dissolved in 70 c.c. of distilled water in the round bottomed flask A. 100 gms. of pure granulated zinc was shaken with 100 c.c. of 0.01 M copper sulphate solution in a 250 c.c. flask for 5 minutes, so as to form a fine coating of copper over the zinc granules. This was then decanted and transfered to the flask A. (The reaction was very slow with only zinc and hydrochloric acid). 140 c.c. of pure distilled concentrated hydrochloric acid was then added dropwise from the funnel T_1. The chromic chloride was thus slowly reduced to deep blue chromous solution. The stopcock P_1 was then closed and a current of carbon dioxide (purified by bubbling through wash bottles containing chromous chloride solution and water) was passed through the flask G to displace the air completely, by opening P_3. When all the chromic chloride was reduced to a deep blue solution and the evolution of hydrogen became quite slow(when the acid in the flask was almost completely exhausted; this took about 2½-3 hours), P_2 was closed and P_1 opened. The pressure of hydrogen in the flask forced the clear blue solution to the flask G through the filter F_1(diameter 1 cm) loosely packed with glass wool. A slow current of carbon dioxide was maintained throughout the operation.

168 gms. of pure hydrated sodium acetate dissolved in 200 c.c. of air free distilled water was added slowly through the

FIG. 1

funnel T. The mixture in the flask was stirred with the help of stirring-cum-filtering arrangement as shown in the diagram. After the complete addition of sodium acetate, stirring was stopped and the red precipitate of chromous acetate allowed to settle. The flask was kept in an ice bath inorder to allow the least amount of the acetate to go into solution.

The precipitate which contained the zinc salt was washed several times with ice cold air free distilled water by connecting the stirrer to the flask J with rubber tubing till the ppt. was free from zinc. (About 10 to 12 washings were necessary for the complete removal of zinc).

The washed chromous acetate was then converted to chromous chloride in the same flask. Since the chromous chloride was to be used in solution as such for the experiments, the precipitate was dissolved in the minimum quantity of cold 1 N hydrochloric acid free from dissolved air. The clear deep blue solution thus obtained was transfered to the storage flask.

Chromous chloride solution free from acetic acid:

The solution prepared by dissolving the acetate in hydrochloric acid always contains an equivalent amount of acetic acid as a product of the reaction. Hence, whenever a completely 'neutral' solution of chromous chloride was required, the following procedure was adopted.

To the resulting solution of chromous chloride containing acetic acid, twice its volume of freshly distilled ice cold alcohol was added when copious precipitate of chromous chloride separated. It was filtered by suction and repeatedly washed with 90% alsohol

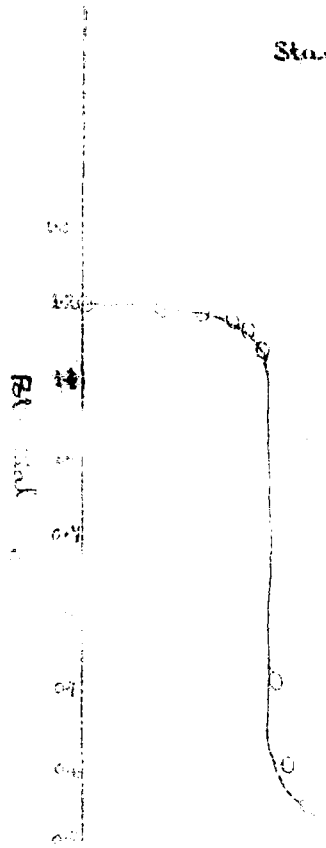
and then with a little of petroleum ether. The latter was then completely expelled by a current of carbon dioxide. The precipitate was then dissolved in the required quantity of ice cold air free distilled water to give the deep blue chromous chloride solution completely free from foreign ions. This improved method of preparation of chromous chloride gave the purest sample of the aquous solution.

Standardisation of the solution:

During the course of these investigations the concentration of chromous chloride and the chromicchromous ratio in various samples had to be dtermined at different intervals. A quick and accurate method whereby chromous chloride could be estimated was sought for. The methods of using potassium dichromate or copper sulphate for the potentiometric estimation of Cr(ii) as recommended by Zintl and Rienacker[1], and Buehrer and Schupp[17], were first of all tried. Both these methods were found to have some limitations and therefore, the following method was devised:

The method depends on the oxidation of chromous chloride by potassium permanganate and titrating the excess of the latter against ferrous iron potentiometrically. 5.0 c.c.of 0.1 N potassium permanganate solution acidified with 20 c.c. of 4 N sulphuric acid was taken in a 100 c.c. beaker and covered with a layer of kerosene (0.5 cm. thick). 2.0 c.c. of chromous solution was then transferred to the permangante keeping the tip of the burette (or pipette when the sample was from a reaction cell) under the layer of kerosene. The mixture was stirred and kept aside for 2-3 minutes (to ensure complete oxidation of Cr(ii)) and then titrated potentiometrically against 0.1 N ferrous ammonium sulphate. Tinsley vernier

Standardis[illegible] boride solution



sulphate solution

potentiometer(type 3387 B) and a smooth platinum wire indicator electrode in conjunction with a Beckmann fibre type calomel electrode were used for the experiment. The readings for one such titration are given below:

T A B L E - 1

Volume of $KMnO_4$ = 5.0 c.c. Volume of $CrCl_2$ = 2.0 c.c.

Volume of $FeSO_4$ (in c.c.)	Potential (vs, S.C.E. in volts)
0.0	1.194
0.5	1.185
0.8	1.180
1.0	1.170
1.1	1.161
1.2	1.130
1.3	0.710
1.4	0.590
1.5	0.540
2.0	0.490

The titre value from the curve = 1.25 c.c.

The strenght of chromous chloride was calculated as follows:

Volume of ferrous ammonium sulphate equivalent to unused permanganate = 1.25 c.c.

Volume of ferrous solution equivalent to the total permanganate used(from potentiometric titration = 4.81 c.c.

Volume equivalent to permanganate used up by chromous chloride solution = 3.56 c.c.

Therefore, strenght of ferrous solution = $\frac{5 \times 0.1}{4.81}$

Strenght of chromous chloride = $\frac{3.56 \times 5 \times 0.1}{4.81 \times 2.0}$ = 0.1850 N

This method was found to be more convenient than the methods usually recommended for the standardisation of chromous

FIG. 2 → GRAVITY TYPE APPARATUS

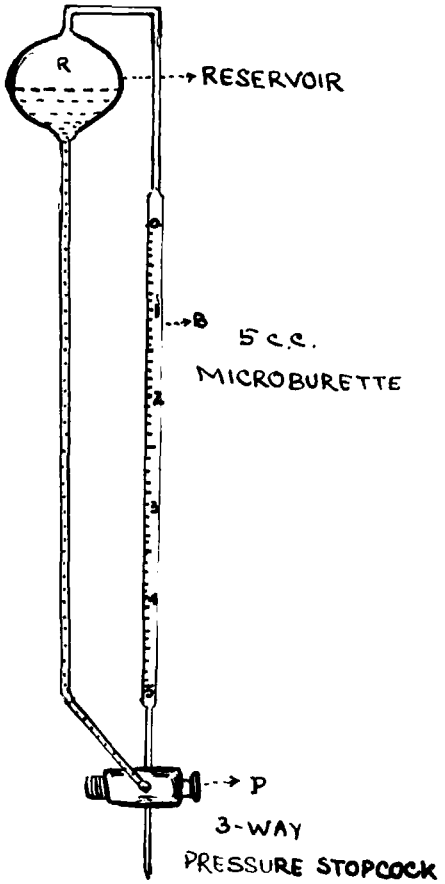
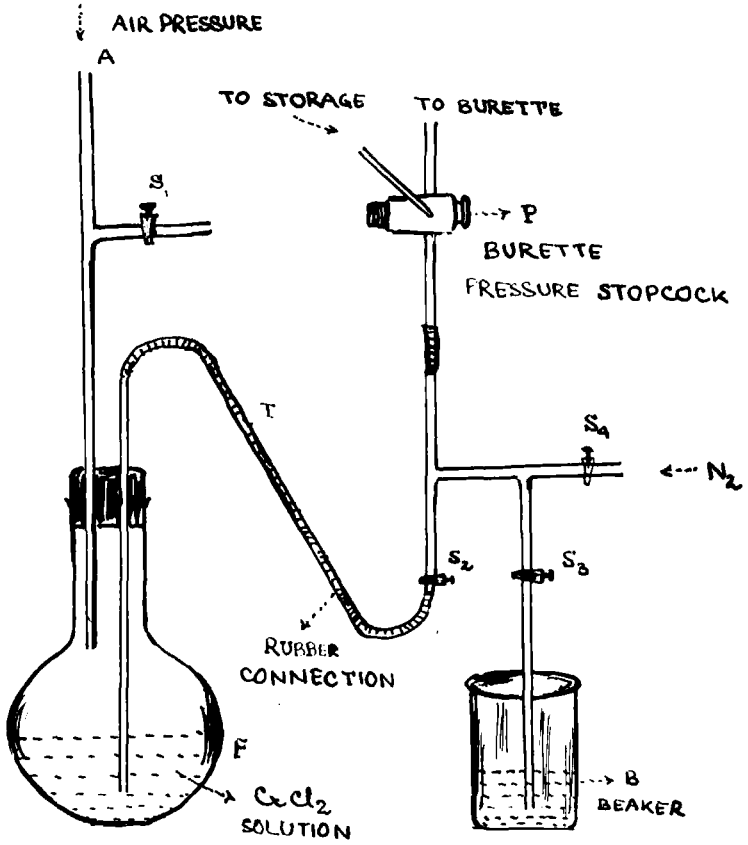


FIG. 3 → BURETTE-FILLING ARRANGEMENT



chloride solution, since it requires neither the maintenance of inert atmosphere nor a special titration cell. Another special advantage is that the deposition of foreign material(such as copper when using copper sulphate) does not affect the performance of the platinum electrode. The accuracy of the method can be judged from the fact that the end point is quite sharp, the fall in potential being 0.6 to 0.65 volt.

Estimation of total chromium for the determination of chromic-chromous ratio.

To determine the total chromium concentration, the method adopted by Forbes and Richter[9] with some modification was followed. A known volume of the solution(2-3 c.c.) was transferred to a conical flask (150 c.c.) and 4-5 gms. of sodium peroxide added to it. 50 c.c. of water was added to this paste after ten minutes and the whole solution was boiled for about 45 minutes to decompose the excess of sodium peroxide. It was then cooled, 10-12 gms. of potassium hydrogen sulphate was added and then boiled to remove the last traces of the peroxide. This was then acidified with sulphuric acid after cooling and titrated iodometrically against sodium thiosulphate or potentiometrically against ferrous ammonium sulphate. The latter method was found to be more accurate.

Storage of chromous chloride solution:

The storage of chromous chloride solution presents difficulties due to high sensitivity towards oxidation. Bucher and Schupp covered the solution with a layer of kerosene and kept under inert atmosphere in a reagent bottle. They found that the

strength of a decinormal solution decreased only by about 1.2% in eight days, but from experience it was found that unless maximum precautions are taken during transfering and keeping the inert atmosphere by a continuous current of carbon dioxide or nitrogen. The rate of oxidation was greater in the beginning and after about twelve days the solution started changing its colour from deep B. blue to bluish green.

A number of devices for storing chromous chloride solution have been recommended. The automatic burette and storage vessel as recommended by Zintl and Rienacker[1] or that designed by Thornton and Chapman[19] is usually taken to be effective in preventing the solution from oxidation. Lingane and Pecsok[4] prepared standard solutions of chromous chloride by reducing pure dichromate with hydrogen peroxide and stored in a flask containing amalgamated zinc. The solution secured in this way was stable for about a week, but the zinc gradually reduced the $H^{\bullet}$ ion concentration thereby resulting in the precipitation of $Cr(OH)_2$. This procedure of storing was also not found satisfactory in this case since it introduced foreign ions in the solution. Storage over aluminium turnings also had the same difficulty.

The storage apparatus devised by M.W.Stone[6] was found the most suitable for preserving chromous chloride solution. The apparatus(fig. 2) consists of a reservoir of 1000 c.c. capacity, the top of which is joined to a microburette B of 5 c.c.(graduated in 0.01 c.c.). The bottom of the reservoir and the other end

of the burette are joined through a three way pressure stopcock P. The top level of the burette was adjusted in such a way that complete solution could be utilized by gravity flow.

The apparatus for introducing the solution into the storage bottle is shown in fig. 3. The stopcock at the top of the fig. corresponds to P of fig. 2. S_1, S_2, S_3 and S_4 are stopcocks and the flask F contains the freshly prepared chromous chloride solution kept under a layer of liquid paraffin .

At the start S_1 and S_4 were closed while S_2 and S_3 were kept open. Air was pumped through the open end A of the tube allowing the chromous chloride solution to pass through the tube T into a beaker B. The stopcock P was then opened and S_3 closed, causing the solution to flow into the reservoir . The rate of flow was manipulated by adjusting S_1. When sufficient chromous chloride had been introduced into the burette and reservoir to absorb all the oxygen, both P and S_2 were closed. The apparatus was then shaken for complete removal of oxygen. This operation reduced the pressure in the reservoir so that it was necessary to introduce additional nitrogen to make up for the loss in pressure. This was done by opening P and S_4 and allowing N_2 (purified by passing through $CrCl_2$) to enter the apparatus. P and S_4 were again closed and the apparatus once more shaken.

Now inorder to clear the storage flask of the prtially oxidised chromous chloride and the excess of nitrogen, S_3 was opened. By this operation the pressure in the apparatus was reduced to approximately one atmosphere. The whole process was repeated

once again to ensure the removal of even the last traces of oxygen. The apparatus was then ready to recieve the solution and this was accomplished by closing S_3, opening S_2 and S_1 and forcing the reagent by pumping air through A. The apparatus was not filled to more than half to avoid any danger due to excess pressure inside. When half filled, the nitrogen would have a pressure of about two atmospheres.

Rubber connections were avoided in the storage apparatus to prevent any possible diffusion of oxygen. For convenience of titration and transfering the solution, a capillary was attached to the tip of the burette with a rubber connection whenever required. The tip of the capillary was kept under the layer of kerosene while transfering the solution.

The strength of the solution was checked from time to time (once in a week) and it was found that the solution remained stable for many months without any change in concentration.

Some properties of the solution:

Chromous chloride solution prepared by the reduction with zinc and hydrochloric acid showed the following properties.

1. Oxidation by atmospheric oxygen: The solution turned greenish violet in no time on exposure to air, but if it contained excess of acid (HCl or H_2SO_4) the colour turned green. The reducing power of the solution was so greatthat it even decomposed water in presence of excess of hydrogen ions and a catalyst like platinum black. In the course of E.M.F. measurements with platinum electrode using excess of hydrochloric acid, the hydrogen evolution was even

visible. Due to its high efficiency to remove even traces of oxygen, the solution was used to purify carbon dioxide and nitrogen for the experiments. These observations are supported by the work of H.W.Stone[20], Traube and Lange[21], Asmanoff[22] and Doring[23]. The differences in colour of the oxidised product might be due to different isomeric forms of Cr(iii), depending on the hydrogen ion concentration and the presence of foreign ions (vide chapter 2,4).

2. Reaction with Alkalis: Sodium hydroxide gave precipitates of a variety of colours depending on the concentration of the alkali and the period of standing . Very dilute solutions of sodium hydroxide gave a brown precipitate while a solution of about 1 N gave a brownish violet precipitate; a still stronger alkali resulted in the formation of a gelatinous precipitate and a dark brown precipitate was obtained with a more concentrated (12 N) sodium hydroxide. These precipitates changed their colours on standing. The different shades of the precipitates may be due to differences in the hydration and particle size as suggested by Hume and Stone[24]. Ammonium hydroxide gave a pale blue precipitate with a visible evolution of small bubbles of hydrogen, the supernatent liquid which was blue also turned reddish violet in air. It is well known that both Cr(ii) and Cr(iii) form a number of complexes with ammonia.[25,26]

3 3. Reaction with a few complex forming reagents: Potassium hydrogen phosphate gave a greyish white precipitate which turned dark green on standing. With potassium molybdate a brownish yellow precipitate was obtained while alkali tugstates gave a grey black precipitate. Chromous chloride solution turned reddish violet by

the addition of citric and tartaric acids, probably due to the formation of the complexes soluble in the acid medium. A slow separation of white needle shaped crystals was observed with potassium tartrate ; the supernatant liquid turned dark green. The nature and composition of the precipitate remain still uninvestigated.

It is very intresting to note that while iron and chromium are similar in many respects, their reactions with potassium ferri- and ferrocyanides, are quite contrasting. While Fe(ii) and Fe(iii) react with potassium ferri- and ferrocyanides to give deep blue compounds, Cr(iii) has no visible action at all under ordinary conditions. Chromous chloride gives a yellowish green precipitate with potassium ferrocyanide; Potassium ferricyanide also giving an insoluble complex of almost the same colour. The chromous complex is quite insoluble and highly stable and exhibits colloidal behaviour. This property of the complex has been fully investigated in the chapter on the composition and nature of chromous ferrocyanide.

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vice versa using mixtures of chromous and chromic chlorides, sulphates, fluorides and acetates, and different electrode materials like platinum, copper, tin and silver. He failed to obtain a relationship between the concentration of chromous ions and the observed E.M.F. His results also suffered from lack of constancy and reproducibility. Higher values were obtained with copper, silver and tin than with platinum. He further observed that on adding fresh chromous or chromic salt, the E.M.F. sometimes changed in the wrong direction at first, but afterwards assumed the normal values determined by the equation $E = E_0 - \frac{RT}{nF} \log \frac{Cr(iii)}{Cr(ii)}$. He obtained the following oxidation potential values for the chromous-chromic system with tin electrode: chloride, 0.38; sulphate, 0.33; fluoride, 0.51; the value for sulphate being the lowest.

Forbes and Richter[6] made a comparative study of the use of mercury and platinum electrodes for chromous chloride(obtained by reducing chromic chloride to different stages by a current of hydrogen at high temperature)solution in hydrochloric acid. They observed that the redox potential at the mercury electrode was although higher(by 0.16 V.) than at platinum, it took nearly two days for the attainment of a constant value while the platinum electrode had the advantage of attaining reversibility in about an hours time. They further observed that the temperature at which the solution was prepared had a marked influence on the potential, the value being about 0.1 V. less than when the solution was made above 15°C. Grube and Schlecht[7] used electrolytic chromium and tin electrodes to determine the chromous-chromic potential. Difficulties and variations

CHAPTER

Factors influencing the redox potential of chromous-chromic system.

Introduction:

The redox potential measurements of the chromous-chromic system present a number of difficulties due to (1) the highly unstable nature of the solution ; (ii) the mode of preparation of the solution; (iii) the possibility of the existence of different isomeric forms of chromous- or chromic ions or both; (iv) the influence of the electrode material; (v) the effect of temperature and (vi) the influence of hydrogen and other foreign ions. Attention to some of these factors was drawn by a number of workers.

As early as 1886 Case[1] and later Skimmer(1896)[2] studied a cell consisting of tin and platinum poles in chromic chloride solution and obtained different values for E.M.F.(from 0 to 0.44 V.) depending on the temperature. At high temperatures the dissolution of tin with the production of chromous chloride and at low temperatures the re-deposition of tin took place. These authors found that the E.M.F. of the cell varied even on shaking and showed a decrease in values when left in open circuit. Mazzuchelli[3] explained these changes as due, in the first instance, to the action of chromic chloride on tin which took place as a local action even when the cell was on open circuit, producing $CrCl_2$ and $SnCl_2$. The values obtained by them did not agree with the theoretical.

Peters[4] could not obtain constant and reproducible results for chromous chromic system with platinum electrodes. Mazzuchelli[5] investigated the conversion of chromous into chromic ions and

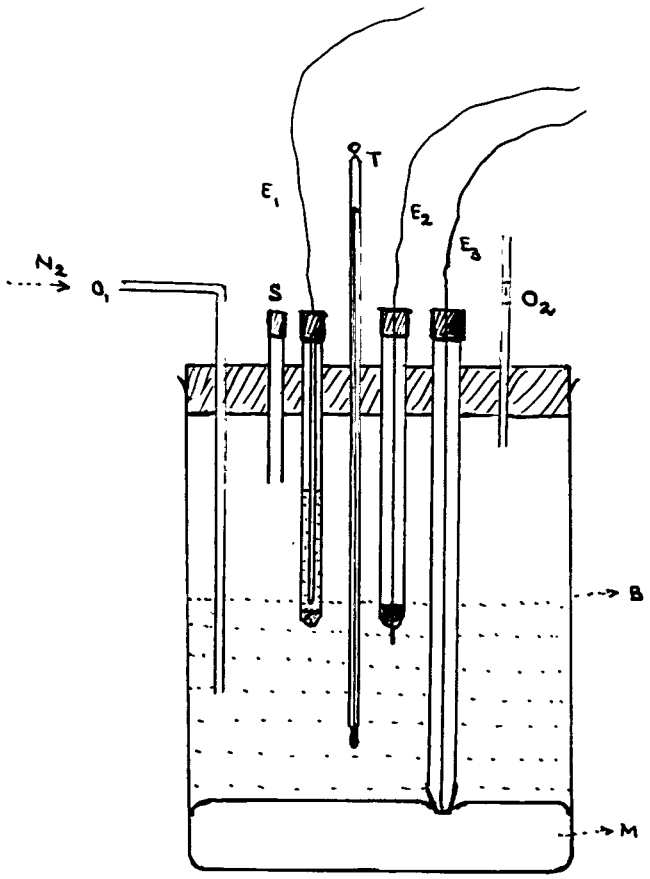
were experienced as a result of catalytic action of the metal surface for the Cr(ii) —— Cr(iii) reaction. They obtained values ranging from 0.38 V. to 0.454 V. under varying conditions of acidity and the nature of the salt(chloride, sulphate or acetate) solution. On further investigation Grube and Breitinger[8] found that the most probable value for the normal potential of chromous-chromic system was 0.412 ± 0.002 V. The potential was measured against a normal calomel electrode using a saturated potassium chloride bridge.

During the course of my preliminary experiments on the application of potential measurements for some of the properties of chromous chloride, it was found necessary to re-investigate the Cr(ii)---Cr(iii) electrode system with a view to ascertain definite conditions essential for obtaining reliable data. From these experiments it could be observed that besides the choice of the electrode material conditions had to be ascertained which should give (i) Steady potential, (ii) rapid equilibrium at the electrode and (iii) a high value for the potential. It may also be of interest to note that so far as I know, almost nothing has been done so far in investigating the redox potential behaviour of the solution as prepared by the reduction of chromic chloride with Zn and HCl. This chapter deals with the observations on the potential of the system as influenced by the use of platinum and mercury electrodes, the presence of nitrogen fumes and under controlled pH.

Apparatus and procedure:

A cell was designed as shown in the fig. 4 for the potential measurements. The mouth of a pyrex beaker(250 c.c.) was cut to

FIG. 4



B .... 250 c.c BEAKER WITH LEVELLED EDGE

O_1 .... N_2 INLET . O_2 .... N_2 OUTLET

M .... MERCURY POOL AS REFERENCE ELECTRODE GIVEN CONNECTION BY PLATINUM ELECTRODE. E_3

T .... THERMOMETER

S .... A SPARE OPENING KEPT CLOSED WHEN NOT IN USE

E_1 .... FIBRE TYPE CALOMEL ELECTRODE

E_2 .... SMOOL PLATINUM ELECTRODE (wire of 1 cm. in length is sealed into a glass tube and given connection via Hg and Cu wire).

level and was fitted with an air tight rubber cork carrying the electrodes, inlet and outlet for the passage of inert gas and a thermometer. Nitrogen was used to expel the air and keep an inert atmosphere in the cell throughout the experiment. A Dunson valve arrangement was used as the outlet for the gas. A Beckmann fibre type calomel electrode was used as the reference, and a platinum electrode to give contact with mercury pool. Another electrode of smooth Platinum wire was also inserted into the cell to be used as the indicator whenever required. A spare hole was left corked for the occasional use to take out or add samples of solutions. The current of nitrogen was maintained throughout and besides this the sample solution was also covered with a layer of kerosene.

The sets of readings were taken first of all using platinum and mercury electrodes seperately by noting the potential with the cell combination mentioned. Only the electrodes(Pt and calomel or Hg and calomel) in use were kept in the cell, the other being removed or kept out of contact with the solution. 'Neutral' solution of chromous chloride was prepared and its strength and total chromium content determined as described in chapter 1 page 12.

30.0 c.c. of distilled air free water was taken in the cell and covered with a layer of kerosene. The air was then completely expelled by passing nitrogen for about half an hour and 30.0c.c. of chromous chloride solution was transferred from the storage flask into the cell by opening S and keeping the tip of the burette below the layer of kerosene. (A long narrow jet tube was connected to the burette by rubber tubing.). The strength of the solution in the cell was determined at different intervals and also after the

time when constancy had been attained, by transferring 2.0 c.c. of the solution from the cell to 10.0 c.c. of 0.1 N permanganate acidified with 20 c.c. of 4 N sulphuric acid and titrating the excess permanganate against 0.1 N ferrous ammonium sulphate potentiometrically. The potentials read against S.C.E. were corrected to hydrogen scale by the formula $E_{H} = E_{indicator} + E_{observed} + E_{calomel}$. The standard value for S.C.E. was taken as -0.2415 at 25°C and the temperature correction was made according to the formula $E = -0.2415 + 0.00073(t-25)^{C}$.

Chromic-chromous ratio in the solutions:

Standardisation of chromous chloride solutions:

Volume of $KMnO_4$ taken	=	10.0 c.c.
Volume of chromous chloride added	=	2.0 c.c.
Strength of permanganate	=	0.11 N.
Strength of ferrous ammonium sulphate	=	0.0882 N
Volume of ferrous solution (from titration curve)	=	4.15 c.c.
Volume of ferrous solution equivalent to $KMnO_4$ used up by $CrCl_2$	=	7.05 c.c.

Therefore strength of $CrCl_2$ solution = [illegible] = 0.2432 N

Concentration of Cr(II) in mole./litre = 0.2432, since the eq.wt. of chromium in the reaction is equal to its own molecular weight.

Total chromium:

Volume of the solution used for oxidation	=	1.0 c.c.
Volume of ferrous ammonium sulphate	=	[illegible] c.c.
Concentration of total chromium in mole./litre	=	[illegible] / 1.0 × 3
	=	0.2310.
Chromic-chromous ratio		
Concentration of Cr(III)	=	0.0303 mole/litre
Ratio of Cr(III)/Cr(II) in the original soln.	=	$\frac{0.0303}{0.2432}$ = 0.122

(a) THE INFLUENCE OF ELECTRODE MATERIAL ON THE TIME FOR ATTAINING STEADY POTENTIAL IN NEUTRAL SOLUTION AND THAT CONTAINING $H^{\cdot}$ AND Cl' IONS.

Table II.

The variation in e.m.f. with time using mercury electrode

Volume of chromous chloride added = 30 c.c.

Volume of water initially taken in the cell = 30 c.c.

Strength of $CrCl_2$ solution (checked by restandardisation) = $\frac{0.3462}{2}$ = 0.1731 M

Original Cr(iii)/Cr(ii) ratio = 0.112

Temperature of the experiment = 30°C

Saturated calomel electrode value at this temp. = - 0.2397 V.

Time	Pot. at Hg electrode w.r.to s.c.e.	Single electrode potential	Strength of Cr(ii)
5 mints	0.125	-0.1147	0.1731 M
10 "	0.1985	-0.0412	
20 "	0.234	-0.0057	
30 "	0.2755	0.0358	
45 "	0.3050	0.0653	0.1731 M
1 hour	0.3480	0.1083	
2 hours	0.4235	0.1738	
3 "	0.4710	0.2313	
5 "	0.5100	0.2703	
18 "	0.6215	0.3815	0.1731 M
24 "	0.6700	0.4303	0.1731 M
48 "	0.6905	0.4508	0.1731 M
60 "	0.6880	0.4483	0.1680 M
72 "	0.6865	0.4468	0.1652 M

The maximum potential attained after 48 hours = 0.4508 V

The ratio Cr(iii)/Cr(ii) = 0.1120
(no change in the original ratio)

$$E_o = E + \frac{RT}{nF} \log \frac{Cr(iii)}{Cr(ii)} = 0.4508 + 0.05915 \log 0.112$$
$$= 0.4508 - 0.05624$$
$$= \underline{0.3946 \text{ volt}}.$$

The value of E_o calculated from the maximum potential and the ratio Cr(iii)/Cr(ii) is 0.3946 volt. The solution changes from blue to violet after the completion of the experiment.

TABLE III.

Variations in e.m.f. with time using platinum electrode:

Volume of chromous chloride added = 30 c.c.

Volume of water initially taken in the cell = 30 c.c.

Strength of $CrCl_2$ solution (checked by restaandardisation) $= \frac{0.3462}{2}$ = 0.1731 M

Original Cr(iii)/Cr(ii) ratio = 0.112

Temperature of the experiment = 30°C

S.C.E. value at this temperature = - 0.2397 V.

Time	Pot. at Pt. electrode w.r. to s.c.c.	Single electrode potential	Strength of Cr(ii)
2 mints	0.1105	-0.1292	0.1731 M
5 "	0.350	0.0103	
10 "	0.3510	0.1113	
15 "	0.4490	0.2093	0.1731 M
30 "	0.5405	0.3008	
45 "	0.5610	0.3213	0.1731 M
1½ hours	0.5605	0.3208	
5 "	0.5610	0.3213	
24 "	0.5615	0.3218	0.1731 M
48 "	0.5600	0.3203	0.1680 M

The maximum potential attained after 45 minutes = 0.3213 volt

The ratio Cr(iii)/Cr(ii) (no change in the original value) = 0.1120

E_o calculated from the maximum potential = 0.2656 V.

Inference:

(i) Maximum steady value attained easily for platinum(in 45 minutes) than for mercury(45 hours).

(ii) Maximum potential for mercury was higher by 0.129 volt(0.3946 at Hg.and 0.2656 at Pt.).

Besides measuring the variations in potential at Hg and Pt electrodes, another intresting aspect of the problem was also studied, that is, the determination of the influence of one electrode on the

other. A set of readings was therefore taken under identical conditions while keeping both the electrodes(mercury pool and smooth platinum) in the solution, allowing contact with either of the electrode at the time of measurement.

T A B L E IV.

Variation of e.m.f. with time while keeping both the electrodes in contact with the solution:

Volume of chromous chloride added = 30 c.c.

Volume of water initially taken in the cell = 30 c.c.

Strength of $CrCl_2$ solution (checked by restandardisation) = $\frac{0.3462}{2}$ = 0.1731 M

Original Cr(iii)/Cr(ii) ratio = 0.112

Temperature of the experiment = 30°C

S.C.E. value at this temperature = -0.2397 V.

Time	Pot.w.r.to s.c.e. Hg elec.	Pt elec	Single electrode pot. Hg elec.	Pt elec	strength of Cr(ii)
5 mints	0.1205	0.2455	-0.1192	0.0058	0.1731 M
10 "	0.1980	0.3505	-0.0417	0.1108	
15 "	0.2250	0.4480	0.0147	0.2083	0.1731 M
30 "	0.2745	0.5400	0.0348	0.3003	
45 "	0.3040	0.5615	0.0643	0.3218	0.1731 M
1 Hour	0.3485	0.5610	0.1088	0.3213	
2 Hours	0.4125	0.5615	0.1728	0.3218	0.1731 M
3 "	0.4715	0.5605	0.2318	0.3208	
5 "	0.5080	0.5605	0.2683	0.3208	0.1719 M
18 "	0.6205	0. 5610	0.3808	0.3213	
24 "	0.6705	0.5610	0.4308	0.3210	0.1731 M
48 "	0.6900	0.5615	0.4503	0.3218	0.1731 M
60 "	0.6865	0.5510	0.4468	0.3113	0.1707 M
72 "	0.6850	0.5500	0.4453	0.3103	0.1645 M

		Hg	Pt
Maximum potential attained	=	0.4503 V.	0.3218 V.
Time taken for the attainment of the maximum value	=	48 hours	45 minutes
E_0 calculated	=	0.3948 V.	0.2554 V.

In order to see the influence of disturbances at the electrodes, the above solution was stirred. The variations in potential were as follows:

TABLE V.

Variations in e.m.f. on disturbing the solution in contact with the elctrodes:

Time	Pot.w.r.to s.c.e.		Single electrode pot.		Strength
	Hg elec.	Pt elec.	Hg elec.	Pt elec.	of Cr(ii)
3 mints	0.6045	0.5750	0.3648	0.3353	0.1645 M
10 "	0.6410	0.5645	0.4013	0.3248	
30 "	0.6785	0.5540	0.4388	0.3143	0.1645 M
1 Hour	0.6820	0.5515	0,4423	0.3118	0.1645 M

It is quite intresting to note that on disturbing the mercury surface by shaking the cell or stirring the solution caused a sudden drop in potential at the mercury electrode and a rise at the platinum. This was only a temporary change and the origibal equilibrium was attained after standing for about an hour (vide the last readings in table iv).

With aview to see the influence of dilution on the e.m.f. at either of the electrodes, readings were taken with the undiluted original solution. 30 c.c. of the solution was transferred from the storage flask into the cell. Variations in the e.m.f. recorded below also include some of the readings for the solution when disturbed by shaking.

T A B L E VI.

Variations in e.m.f. with time with the undiluted solution:

Volume of chromous chloride taken = 30 c.c.

Strength of the solution(original) = 0.3462 M

Ratio of Cr(iii)/Cr(ii) = 0.112

Value of s.c.e($31^{o}C$) = -0.2369

Time	Pot.w.r.to s.c.e.		Single electrode pot.		Strength
	Hg elec.	Pt elec.	Hg elec.	Pt elec.	of Cr(ii)
5 Mints	0.4190	0.5425	0.1921	0.3056	0.3438 M
10 "	0.5155	0.5620	0.2786	0.3251	
30 "	0.5900	0.5620	0.3531	0.3251	
1 Hour	0.6320	0.5645	0.3951	0.3276	0.3438 M
Disturbed	0.5340	0.5710	0.2921	0.3341	
2 Hours	0.6710	0.5615	0.4341	0.3246	
5 "	0.6865	0.5680	0.4496	0.3251	0.3414 M
Disturbed	0.6030	0.5700	0.3461	0.3331	
18 Hours	0.6910	0.5610	0.4541	0.3241	0.3438 M
Disturbed	0.5930	0.5695	0.3561	0.3326	
24 Hours	0.6915	0.5615	0.4546	0.3246	
Disturbed	0.5930	0.5690	0.3561	0.3321	
36 Hours	0.6870	0.5600	0.4501	0.3231	
48 "	0.6875	0.5610	0.4506	0.3241	0.3414 M
Disturbed	0.5950	0.5695	0.3581	0.3326	
60 Hours	0.6880	0.5590	0.4511	0.3221	0.3280 M

(The solution became violet at the end of the experiment)

		Hg	Pt
Maximum potential attained	=	0.4546 V.	0.3251 V.
E_o calculated	=	0.3986 V.	0.2691 V.

Inference:

High potential reached with more concentrated solution. The potential takes lesser time to attain constancy(Pt, 10 minutes; Hg, 24 hours).

Besides the concentration of chromous chloride solution, the presence of acids and neutral salts is also likely to influence the e.m.f. at the electrodes. The following setsof readings were, therefore, taken in presence of potassium chloride and hydrochloric acid in order to see the effect of hydrogen and chloride ions.

TABLE VII.

Variation in e.m.f. with time with solution containing KCl.(1.5 N)

Time	Pot.w.r.to s.c.e.		Single electrode pot.		Strength of Cr(ii)
	Hg elec.	Pt elec.	Hg elec.	Pt elec.	
5 Mints	0.2550	0.2145	0.0153	-0.0252	0.1719 M
10 "	0.3050	0.3210	0.0653	0.0813	
15 "	0.3475	0.4475	0.1078	0.2078	
30 "	0.3600	0.5600	0.1203	0.3203	0.1719 M
45 "	0.3950	0.5925	0.1553	0.3528	
1 Hour	0.4265	0.6110	0.1868	0.3713	
2 Hours	0.4700	0.6115	0.2303	0.3718	0.1707 M
3 "	0.5300	0.6110	0.2903	0.3713	
5 "	0.5980	0.6115	0.3583	0.3718	
8 "	0.6435	0.6115	0.4038	0.3718	0.1707 M
28 "	0.7100	0.6105	0.4803	0.3708	
48 "	0.7500	0.6110	0.5103	0.3713	0.1645 M
60 "	0,7490	0.6000	0.5093	0.3603	
72 "	0.7475	0.5890	0.5078	0.3493	0.1600 M

		Hg elec.	Pt elec.
Maximum values attained	=	0.5103 V.	0.3718 V.
E_0 values calculatrd	=	0.4639 V.	0.3189 V.

Inference:

1. Time taken to attain constancy was less than in the case of neutral solution.

2. The difference in potential at the two electrodes was higher than for the solution without KCl (0.1285 without KCl and 0.1385 in presence of KCl)

3. Higher maximum values attained(without KCl, 0.4503 at Hg and 0.3218 at Pt); with KCl, 0.5103 and 0.3718 at Hg and Pt respectively).

The observations were repeated under similar conditions, taking 3 N hydrochloric acid in place of potassium chloride. The readings are entered as below:

T A B L E VIII.

Variation in e.m.f. with time with solution containing 3 N HCl.

Total chromium concentration in the sample = 0.1925 N.

Time	Pot.w.r.to s.c.e.		Single electrode pot.		Strength of Cr(II)
	Hg elec.	Pt elec.	Hg elec.	Pt elec.	
5 Mints	0.2540	0.2300	0.0143	-0.0097	0.1719 N
10 "	0.3100	0.2750	0.0703	0.0353	
15 "	0.3480	0.4800	0.1033	0.2403	
30 "	0.3610	0.6000	0.1213	0.3603	0.1707 N
45 "	0.3970	0.6435	0.1573	0.4038	
1 Hour	0.4280	0.6500	0.1983	0.4103	
2 Hours	0.4725	0.6300	0.2328	0.4203	0.1707 N
3 "	0.5300	0.6535	0.2903	0.4138	
5 "	0.5905	0.6530	0.3523	0.4133	
18 "	0.6440	0.6520	0.4043	0.4123	0.1645 N
23 "	0.7050	0.6530	0.4653	0.4133	
48 "	0.7510	0.6400	0.5113	0.4003	0.1645 N
60 "	0.7475	0.6000	0.5078	0.3603	
72 "	0.7470	0.5500	0.5073	0.3103	0.1600 N

		Hg elec.	Pt elec.
Maximum values attained	=	0.5113 V.	0.4203 V.
E_0 values calculated	=	0.4649 V.	0.3674 V.

Inference:

(1). Time taken to attain the maximum potential was almost the same as in presence of KCl.

(2). Maximum potential at the Hg electrode was the same as for KCl, but at platinum the value was higher; so the difference in ptential at the two electrodes was small as compared with KCl (vide table VIII).

(3). Stirring the solution had no effect on the potential of the solution containing HCl or KCl although neutral solution was effected.

Since under different conditions a difference of 0.13 to 0.14 V. was observed between the potential values at the two electrodes, a set of readings were taken with W, Pt and Hg electrodes with a view to ascertain whether the material of the electrode is responsible for the difference or the surface of the electrode also effects the values.

T A B L E X.

Variation in e.m.f. with the three electrodes(W, Pt and Hg) dipped in solution, allowing contact with only one at the time of measurement.

Volume of chromous chloride solution taken = 30.0 c.c.

Strength of the solution = 0.3414 M

Time	Pot.w.r.to s.c.e.			Single electrode pot.			Strength of Cr(ii)
	Pt	W	Hg	Pt	W	Hg	
5 Mints	0.5400	0.5185	0.4100	0.3003	0.2788	0.1703	0.3414 M
10 "	0.5570	0.5470	0.5085	0.3173	0.3073	0.2688	
30 "	0.5625	0.5580	0.5840	0.3228	0.3183	0.3443	
1 Hour	0.5625	0.5600	0.6230	0.3228	0.3203	0.3833	0.3414 M
2 Hours	0.5620	0.5600	0.6675	0.3223	0.3203	0.4278	
5 "	0.5610	0.5600	0.6310	0.3213	0.3203	0.4413	0.3414 M
Stirred	0.5700	0.5690	0.6185	0.3303	0.3293	0.3788	
18 Hours	0.5590	0.5585	0.6850	0.3193	0.3188	0.4453	
23 "	0.5575	0.5575	0.6855	0.3178	0.3178	0.4458	0.3400 M
36 "	0.5525	0.5540	0.6840	0.3128	0.3163	0.4443	
48 "	0.5525	0.5500	0.6840	0.3128	0.3103	0.4443	0.3280 M
Stirred	0.5610	0.5600	0.6120	0.3213	0.3203	0.3723	
60 "	0.5410	0.5455	0.6820	0.3013	0.3058	0.4423	

		Pt	W	Hg
Maximum potential attained	=	0.3228V.	0.3203V.	0.4458 V.
E_o calculated	=	0.2665V.	0.2640V.	0.3895 V.
Time of constancy	=	30 mins	45 mins	24 hrs

Inference.

(1). Potential values were almost the same at Pt and W electrodes

(2). From the above table it is evident that a smooth Pt electrode can be advantageously used for studying the chromous-chromic redox system and sufficient time should be allowed before taking the reading so that a steady value is reached.

Summary of the results regadring the influence of electrodes on the e.m.f. values:

T A B L E XI.

Medium or conditions	Calculated values of E_o		Time for attaining steady potential	
	Pt	Hg	Pt	Hg
Original solution	0.2691	0.3986	10 minutes	24 Hours
Solution diluted twice in the cell	0.2554	0.3948	45 "	43 "
Solution twice diluted with 3 N KCl	0.3189	0.4639	45 "	48 "
Solution twice diluted with 3 N HCl	0.3674	0.4649	45 "	48 "
Original solution saturated with KCl	0.3243	0.4678	30 "	18 "

Inference:

(1). While the influence of KCl and HCl on the potential at the mercury electrode are almost the same, HCl has a greater influence at Pt than at Hg electrode.

(2). E_o values calculated for dilute solutions are less than for the original solution(undiluted).

(3). The time taken for attaining the steady value is less in the case of original solution and in presence of saturated KCl.

(b) THE INFLUENCE OF DILUTION, ADDITION OF ACIDS, BASES AND SALTS AND DIFFERENT VARIETIES OF CHROMIC CHLORIDE ON THE REDOX POTENTIAL MEASUREMENTS USING PLATINUM ELECTRODE.

A fresh 'neutral' sample of chromous chloride solution was prepared and transferred to the storage flask. The solution was standardised after two days (since the strength varied slightly

in the begining and came to a constant value after two days period) by the back estimation method using potassium permanganate and ferrous ammunium sulphate (vide page 12). The readings are given below:

Volume of potassium permanganate taken	= 10.0 c.c.
Volume of chromous chloride added	= 2.0 c.c.
Strength of permanganate solution	= 0.105 N
Strength of ferrous ammonium sulphate (potentiometrically determined)	= 0.0955 N
Volume of ferrous solution required to reduce the excess permanganate	= 3.55 c.c.
Volume of ferrous solution equivalent to the total permanganate taken	= 11.0 c.c.
Volume of ferrous solution equivalent to the permanganate used up by chromous chloride	= 7.45 c.c.
Strength of chromous chloride solution	= 0.3558 M

Total chromium in the sample:

Volume of solution used for oxidation	= 1.0 c.c.
Volume of ferrous ammonium sulphate required to reduce the dichromate formed(determined potentiometrically)	= 12.15 c.c.
Concentration of total chromium in moles/liter	= 0,3868
Hence concentration of Cr(iii)	= 0.0310 M
Ratio Cr(iii)/Cr(ii) in the solution	= 0.08414

The influence of dilution on the redox potential of the system was first studied. The dilution of the solution was carried out in the cell by taking air free distilled water and adding chromous chloride, after complete deaeration. The strength of chromous chloride after dilution was determined potentiometrically in each case.

TABLE XII.

Variation in potential with dilution:

NO.	Vol. of $CrCl_2$	Vol. of water	Time	Pot vs s.c.e.	Electrode potential	Strength of $CrCl_2$
1.	30 c.c.	0 c.c.	5 mints	0.5650	0.3253	0.3558 M
			10 "	0.5710	0.3313	
	(original		15 "	0.5710	0.3313	
	solution)		25 "	0.5715	0.3318	
2.	20 c.c.	10 c.c.	5 "	0.2825	0.0428	0.237 M
			10 "	0.3900	0.1503	
	(1.5 times		15 "	0.4710	0.2313	
	diluted)		30 "	0.5515	0.3118	
			1 Hour	0.5510	0.3113	
3.	15 c.c.	15 c.c.	5 mints	0.2300	-0.0097	0.178 M
			10 "	0.3515	0.1118	
	(2 times		20 "	0.4720	0.2323	
	diluted)		30 "	0.5350	0.2953	
			1 Hour	0.5350	0.2953	
4.	10 c.c.	20 c.c.	5 Mints	0.1625	-0.0772	0.118 M
			10 "	0.2900	0.0503	
	(3 times		20 "	0.3955	0.1558	
	diluted)		30 "	0.4610	0.2213	
			1 Hour	0.4620	0.2213	
5.	5 c.c.	25 c.c.	5 mints	0.1015	-0.1382	0.0575 M
			10 "	0.2600	0.0203	
	(6 times		20 "	0.3510	0.1113	
	diluted)		30 "	0.4000	0.1603	
			1 Hour	0.4100	0.1703	
6.	2 c.c.	28 c.c.	5 mints	-0.0050	-0.2447	0.023 M
			10 "	0.1585	-0.0812	
	(15 times		20 "	0.2400	0.0003	
	diluted)		30 "	0.2810	0.0413	
			1 Hour	0.3205	0.0812	
			1½Hours	0.3510	0.1113	
			2 "	0.3515	0.1118	
7.	1 c.c.	29 c.c.	5 mints	-0.1820	-0.2217	0.0114 M
			10 "	-0.0010	-0.2407	
	(30 times		20 "	0.1405	-0.0992	
	diluted)		30 "	0.2060	-0.0337	
			1 Hour	0.2400	0.0003	
			1½Hours	0.2975	0.0578	
			2 "	0.2990	0.0593	

The solution became violet in every case towards the end of the experiment.

TABLE XIII.

Summary of the results for the variation in potential of chromous chloride solution with dilution.

Dilution	Max. potential attained	Time taken for attaining the steady potential
Original soln.	0.3318	10 minutes
1.5 times	0.3118	30 "
2 "	0.2958	30 "
3 "	0.2223	1 Hour
6 "	0.1703	1 "
15 "	0.1110	2 Hours
30 "	0.0593	2 "

Inference:

(1). The chromous-chromic ratio is not affected by dilution - the strength of chromous chloride being directly proportional to the extent of dilution.

(2). Concentration of the solution influences the redox value to a great extent.

(3). Time of the attainment of a steady potential is also influenced by dilution, greater the dilution, larger the time required.

EXPERIMENTAL DETERMINATION OF THE NORMAL POTENTIAL OF CHROMOUS-CHROMIC SYSTEM:

As pointed out earlier, almost very little has been done for determining the E_o value for chromous chloride solution obtained by reducing chromic chloride with Zn and HCl . Attempt was, therefore, made to determine the value of the redox potential for such a chromous-chromic system so as to get more dependable results. Since the presence of acids also influence the E value, determinatio

were carried out in presence of varying amounts of HCl.

The method usually employed for determining E_o is by measuring the potentials of solutions containing the mixture of salts in the various oxidation states of the ion concerned. The standard potential is therefore, obtained either by measuring the potential of the solution containing the two salts in equimolar proportion or by extra-plating the values for the different mixtures to 1:1 ratio. While adopting this procedure it was observed that the addition of chromic chloride brought about an initial reversal of the value in the redox potential, although it came to more or less a steady value after some time. This method was, therefore, found unsuitable and inconvenient for the determinations of E_o . Another method was hence sought for.

Before giving my observations on the determinations of the standard potential, it appears worthwhile to incorporate briefly the results on the effect of the addition of chromic chloride on the potential of chromous solution.

Effect of additon of chromic chloride on the potential of chromous-chromic system.

20.0 c.c. of the original chromous chloride solution was tranferred to the cell after complete replacement of air (by nitrogen) and the potential noted till equilibrium was attained. Taking this potential as the steady and reversible value for the system, aliquots of standard solution (0.1 M) of green chromic chloride were added and the e.m.f. noted with time till constancy was attained in each case.

T A B L E XIV.

Changes in potential by the addition of chromic chloride solution.

Volume of Chromous chloride solution taken = 20.0 c.c.

Initial concentration of the solution = 0.3558 M

Original chromic-chromous ratio = 0.112

Potential of s.c.e. at the temperature of the experiment. = -0.2392 V.

No.	Volume of 0.1 M $CrCl_3$ added	Time	Pot. vs s.c.e.	Electrode potential
1.	0.0 c.c.	5 mints	0.5625	
		10 "	0.5700	
		15 "	0.5710	
		20 "	0.5710	0.3318 V.
2.	2.0 c.c.	5 "	0.5825	
		10 "	0.5780	
		20 "	0.5665	
		30 "	0.5520	
		45 "	0.5465	
		1 Hour	0.5465	0.3073 V.
3.	5.0 c.c.	5 mints	0.5490	
		10 "	0,5430	
		20 "	0.5375	
		30 "	0.5340	
		45 "	0.5340	0.2948 V.
4.	10.0 c.c.	5 "	0.5455	
		10 "	0.5380	
		20 "	0.5315	
		45 "	0.5265	
		1 Hour	0.5265	0.2873 V.

Inference:

(1). The reversal of potential takes place after each addition of chromic chloride solution.

(2). The potential decreases and attains constancy within 45 to 60 minutes.

Several sets of such experiments were carried out by the addition of varying amounts of chromic chloride solution. The potential E_0 was calculated in every case from the observed

e.m.f. and the chromic chromous ratio. A summary of the results is given in the table below:

TABLE XV.

E_o value obtained by changing the composition of chromous-chromic mixture by the addition of chromic chloride solution.

Conc.of Cr(ii)	Conc.of Cr(iii)	log $\frac{Cr(iii)}{Cr(ii)}$	$\frac{RT}{nF}$ log$\frac{Cr(iii)}{Cr(ii)}$	Max. Pot.	$E_o$calculated
0.3558	0.0310	-1.0908	-0.0645	0.3318	0.2673
0.3237	0.0732	-0.6465	-0.0382	0.3073	0.2691
0.2855	0.1041	-0.4380	-0.0259	0.2948	0.2689
0.2373	0.1175	-0.3052	-0.0181	0.2873	0.2692
0.2032	0.1270	-0.2041	-0.0121	0.2808	0.2687
0.1780	0.1341	-0.1229	-0.0073	0.2746	0.2675
0.1424	0.1441	0.0053	0.0003	0.2688	0.2691
0.1187	0.1508	0.1038	0.0061	0.2623	0.2684
0.0890	0.1591	0.2523	0.0456	0.2238	0.2694

Inference:

Although there is an initial reversal of potential on the addition of chromic chloride, the average E_o value calculated is almost the same as for the solution without the addition of chromic chloride(the average E_o is equal to 0.2684; vide also page 30).

Titration method for the determination of E_o of the system.

Chromous chloride was titrated against standard potassium dichromate solution; the latter acted as a potential mediator.[10-13] Potentials were measured during the progressive oxidation of chromous chloride and the E_o value calculated at each step.

The potential at the smooth platinum wire electrode was read against a saturated calomel electrode in the air tight cell(vide page 23). 10 c.c. of hydrochloric acid potassium chloride mixture(of varying strengths) was taken in the cell. The air

from the cell was removed by passing a current of purified nitrogen and 10 c.c. of chromous chloride solution was then transferred into the cell. The equilibrium fer potential was read after half an hour. Increasing amounts of 0.1 N potassium dichromate were added from a 25 c.c. standard burette and the readings taken fifteen minutes after each addition. The titration was continued till the end point was reached as indicated by the sudden drop in potential by the addition of a small drop of the titrant.

Let t_c be the volume of the titrant added when the sudden change in potential occurs(i.e.when the oxidation is complete) and t be the amount added at any point in the titration, then at this point 0 , the oxidised form is equivalent to t and r the reduced form will be equivalent to $t_c - t$. On substituting these values in the equation $E = E_o - \frac{RT}{nF} \log \frac{ox.}{red.}$ we get $E = E_o - \frac{RT}{nF} \log \frac{t}{t_c - t}$, where E_o is the normal potential of the system.

Since the chromous chloride solution contained some chromic chloride also, the above equation might be used for determining the potential at various stages after making the necessary correction for the initial amount of Cr(iii) present in the sample. The readings taken for various acid concentrations are entered in the following pages:

Strength of chromous chloride (original)	= 0.3558 M
Strength of chromous chloride in the cell (10 c.c. original solution + 10 c.c. KCl and HCl)	= 0.1779 M
Strength of Cr(iii) solution in the cell	= 0.0155 M
Normality of dichromate solution	= 0.10 N.

Volume of 0.1 N dichromate which would be required for the formation of 20.0 c.c. of 0.0155 M Cr(iii) = 0.31 c.c.

Volume correction applied(Vol. of dichromate) = + 0.31 c.c.

Value for s.e.e.(at 25°C) = 0.2415 V.

T A B L E.XVI.

E_o values at various concentrations of HCl:

Conc. of HCl	Vol. of 0.1 N $K_2Cr_2O_7$	Percentage of Cr(iii)	Pot.obs vs.s.c.e	Elec. Pot.	Log $\frac{Cr(iii)}{Cr(ii)}$	E_o^{**} Calculated
0.05 N	0.0c.c.	0.87	0.5860	0.3445	-1.0598	0.2818
	5.0 "	14.77	0.5680	0.3265	-0.7614	0.2815
*	10.0 "	29.36	0.5460	0.3045	-0.3954	0.2811
(KCl 1.95 N)	15.0 "	42.62	0.5315	0.2900	-0.1292	0.2824
	20.0 "	56.54	0.5165	0.2750	+0.1144	0.2818
	25.0 "	70.47	0.4900	0.2585	0.3778	0.2809
	30.0 "	84.39	0.4795	0.2380	0.7332	0.2814
	35.6 "	100.00	(-0.4150)		-	-
	0.0 "	0.87	0.5980	0.3565	-1.0598	0.2938
0.1 N	5.0 "	14.77	0.5795	0.3380	-0.7614	0.2930
	10.0 "	29.36	0.5585	0.3170	-0.3954	0.2936
(KCl 1.9 N)	15.0 "	42.62	0.5435	0.3020	-0.1292	0.2944
	20.0 "	56.54	0.5285	0.2870	0.1144	0.2938
	25.0 "	70.47	0.5155	0.2710	0.3778	0.2934
	30.0 "	84.39	0.4915	0.2500	0.7332	0.2934
	35.6 "	100.00	(-0.4300)		-	-
	0.0 "	0.87	0.6180	0.3765	-1.0598	0.3138
0.2 N	5.0 "	14.77	0.5995	0.3580	-0.7614	0.3130
	10.0 "	29.36	0.5780	0.3365	-0.3954	0.3129
(KCl 1.8 N)	15.0"	42.62	0.5630	0.3215	-0.1292	0.3139
	20.0 "	56.54	0.5470	0.3055	0.1144	0.3123
	25.0 "	70.47	0.5325	0.2910	0.3778	0.3134
	30.0 "	84.39	0.5115	0.2700	0.7332	0.3134
	35.6 "	100.00	(-0.4850)		-	-
	0.0 "	0.87	0.6470	0.4055	-1.0598	0.3428
0.5 N	5.0 "	14.77	0.6295	0.3880	-0.7614	0.3430
	10.0 "	29.36	0.6075	0.3660	-0.3954	0.3426
(KCl 1.5 N)	15.0"	42.62	0.5915	0.3500	-0.1292	0.3424
	20.0 "	56.54	0.5780	0.3365	0.1144	0.3437
	25.0 "	70.47	0.5610	0.3195	0.3778	0.3419
	30.0 "	84.39	0.5415	0.3000	0.7332	0.3434
	35.6" "	100.00	(-0.5050)		-	-

Contd..

Conc. of HCl	Vol. of 0.1 N $K_2Cr_2O_7$	Percentage of Cr(iii)	Pot. obs. vs. s.c.e.	Elec. Pot.	Log $\frac{Cr(iii)}{Cr(ii)}$	E_o** calculated.
0.8 N	0.0 c.c.	0.87	0.6615	0.4200	-1.0598	0.3573
	5.0 "	14.77	0.6430	0.4015	-0.7614	0.3565
(KCl 1.2 N)	10.0 "	29.36	0.6225	0.3810	-0.3954	0.3576
	15.0 "	42.62	0.6060	0.3645	-0.1292	0.3569
	20.0 "	56.54	0.5920	0.3505	0.1144	0.3573
	25.0 "	70.47	0.5715	0.3340	0.3778	0.3564
	30.0 "	84.39	0.5550	0.3135	0.7332	0.3569
	35.6 "	100.00	(-0.5055)		-	-
	0.0					
1.0 N	5.0 "	0.87	0.6675	0.4260	-1.0598	0.3633
	10.0 "	14.77	0.6490	0.4075	-0.7414	0.3625
(KCl 1.0 N)	15.0 "	29.36	0.6275	0.3860	-0.3954	0.3626
	20.0 "	42.62	0.6120	0.3705	-0.1292	0.3629
	25.0 "	56.54	0.5980	0.3565	0.1144	0.3633
	30.0 "	70.47	0.5820	0.3405	0.3778	0.3629
	35.6 "	84.39	0.5605	0.3190	0.7332	0.3624
		100.00	(-0.5100)		-	-
1.5 N	0.0 "	0.87	0.6705	0.4290	-1.0598	0.3663
	5.0 "	14.77	0.6535	0.4120	-0.7414	0.3670
(KCl 0.5 N)	10.0 "	29.36	0.6320	0.3905	-0.3954	0.3671
	15.0 "	42.62	0.6150	0.3735	-0.1292	0.3659
	20.0 "	56.54	0.6010	0.3595	0.1144	0.3663
	25.0 "	70.47	0.5865	0.3450	0.3778	0.3674
	30.0 "	84.39	0.5640	0.3225	0.7332	0.3659
	35.6 "	100.00	(-0.5650)		-	-
2.0 N	0.0 "	0.87	0.6730	0.4315	-1.0598	0.3688
	5.0 "	14.77	0.6540	0.4125	-0.7614	0.3675
	10.0 "	29.36	0.6330	0.3915	-0.3954	0.3681
	15.0 "	42.62	0.6175	0.3760	-0.1292	0.3684
	20.0 "	56.54	0.6030	0.3615	0.1144	0.3683
	25.0 "	70.47	0.5875	0.3460	0.3778	0.3684
	30.0 "	84.39	0.5660	0.3245	0.7332	0.3679
	35.6 "	100.00	(-0.5635)		-	-

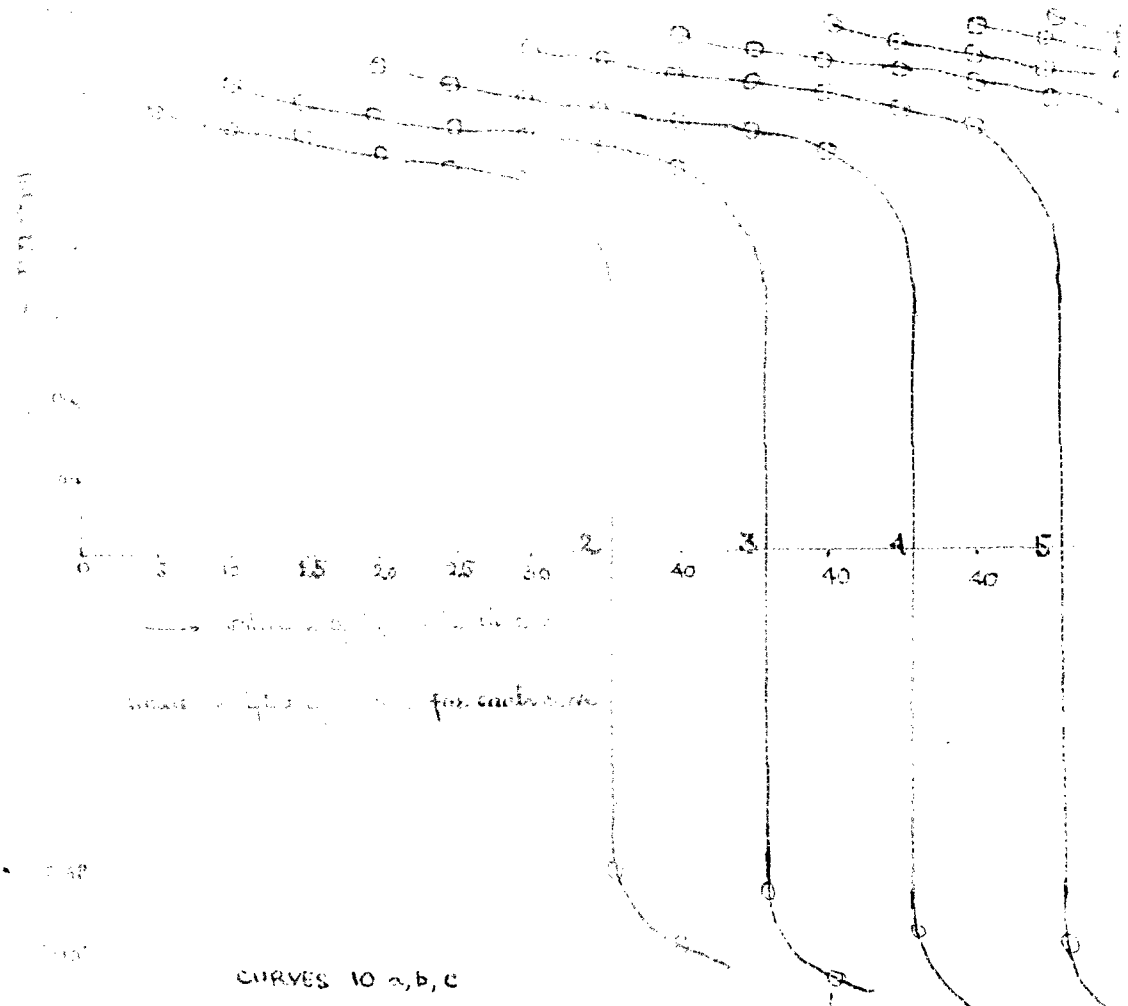
* The concentration of chloride ion was kept constant by the addition of necessary amount of potassium chloride solution.

** E_o was calculated from the equation $E = E_o - \frac{RT}{nF} \log \frac{t}{t_c - t}$ (vide page 42).

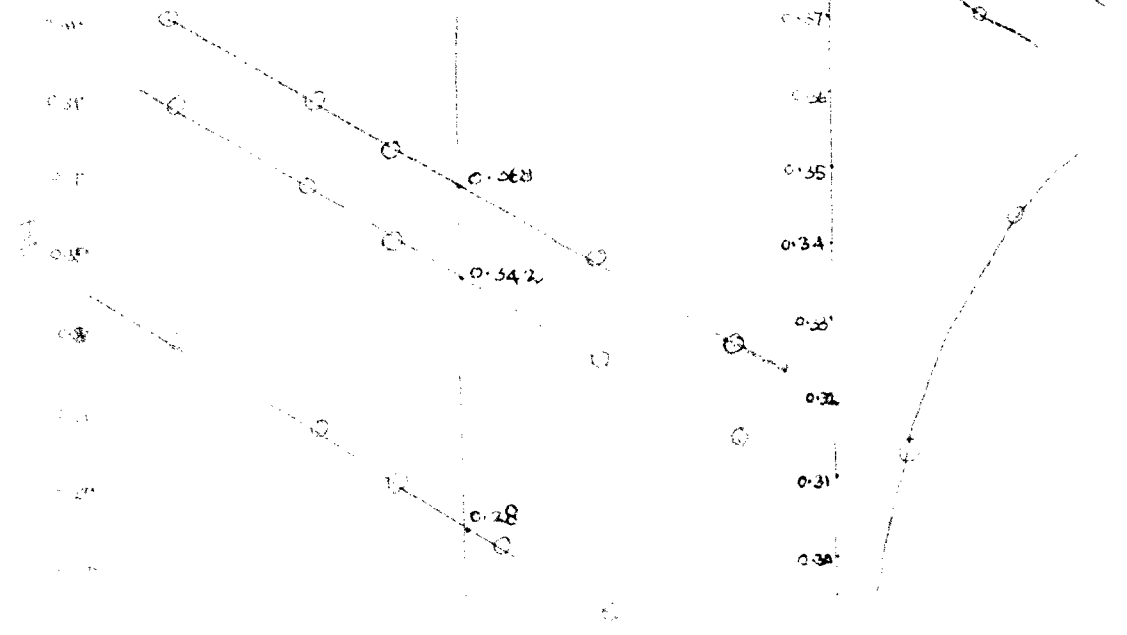
The value of t_c is equal to volume of dichromate required for complete oxidation plus 0.31, and t is equal to the volume added at any stage plus 0.31.

CURVES 2 to 9

TITRATION OF $CaCl_2 \times K_2Cr_2O_7$



CURVES 10 a, b, c



The titration with zero acid concentration was found very difficult since the electrodes became quite insensitive and also equilibrium was not attained even after one hour after each addition of dichromate solution. The following table give the summary of the changes in the normal potential with the concentration of hydrochloric acid-

TABLE XVII

Changes in potential with concentration of HCl:

Total chromium concentration	Concentration of HCl	Average E_o (volt)
0.1934 moles/litre	0.05 N	0.2816
" "	0.10 N	0.2936
" "	0.20 N	0.3102
" "	0.50 N	0.3423
" "	0.80 N	0.3570
" "	1.00 N	0.3623
" "	1.50 N	0.3660
" "	2.00 N	0.3682

It is seen from the above table that the value for the normal potential rises with the concentration of the acid and reaches more or less a constant value when the strength of the acid/solution is about 2.00 N. The normal potential calculated in neutral medium by direct measurements is 0.2684 and the difference between this value and the maximum attained in presence of acid is found to be 0.1 Volt (0,3682-0.2684) approximately.

The value of log $\frac{ox.}{red}$ was plotted against the electrode potentials (vide curve no) at variou acid concentrations and parellel straight lines were obtained having a slope 0.057. This value, according to the equation $E = E_o - \frac{RT}{nF} \log \frac{ox.}{red}$., is in agreement with a one electron reaction, i.e. forthe value n =1.

Further, the normal potential of the system (E_o) at the various acid concentrations are obtained by the points at which the ratio $\frac{ox.}{red}$ is unity or log. $\frac{ox.}{red}$ is zero.

A graph was plotted between the E_o values and the concentration of hydrochloric acid(i.e. the concentration of hydrogen ions approximately) and a curve of the type facing page 45 was obtained. At higher concentrations of HCl (more than 2 N) the curves tends to be a straight line.

The oxidation of chromous chloride solution in neutral and in acid media were also tried using hydrogen peroxide. But on adding hydrogen peroxide the electrodes became quite insensitive probably due to the catalytic decomposition of hydrogen peroxide by platinum and the formation of a layer of small bubbles of oxygen on the elctrode(this was visible in certain cases). The results obtained were the same as in the case of dichromate oxidation, except that the steepness in the curve at the end point was not so pronounced as in the latter case. (A potential jump of 0.6 to 0.7 volt was observed in the case of hydrogen peroxide and about 1 volt in the case of potassium dichromate). One such set of readings with hydrogen peroxide is given in table No. 12.

T A B L E XVIII.

Readings for the titration of chromous chloride against H_2O_2.

Strength of chromous chloride solution(original) = 0.3558 M

Volume of 2 N HCl taken in the cell = 5.0 c.c.

Volume of 2 N KCl taken in the cell = 5.0 c.c.

Volume of $CrCl_2$ transferred into the cell = 10.0 c.c.

Strength of Chromous solution in the cell = 0.1779 M

Concentration of Cr(iii) in the mixture = 0.0155 M

Normality of hydrogen peroxide used = 0.10 N

Value for s.c.e. at the temperature of the Expt.(25°C) = -0.2415

Conc. of HCl-KCl	Vol.of 0.1 N H_2O_2	Cr(iii) percentage	Pot.obs. (vs.s.c.e.)	$\log\frac{Cr(iii)}{Cr(ii)}$	Elec. Pot.	E_o calculated
	0.0 c.c.	0.87	0.6465	-1.0598	0.4050	0.3423
	5.0 "	14.77	0.6290	-0.7614	0.3875	0.3425
0.5 N HCl	10.0 "	29.36	0.6080	-0.3954	0.3665	0.3431
and	15.0 "	42.62	0.5920	-0.1292	0.3505	0.3429
0.5 N KCl	20.0 "	56.54	0.5775	0.1144	0.3360	0.3438
	25.0 "	70.47	0.5600	0.3778	0.3185	0.3429
	30.0 "	80.39	0.5410	0.7332	0.2995	0.3439
	35.6 "	100.00	(-0.1620)	-		▼

Inference:

(1). Average E value calculated = 0.3431 v.

(2). This value is almost the same as that obtained with dichromate in the presence of the same acid concentration(0.3428 volt)

From the titrations of chromous chloride solution against potassium dichromate under various acid concentrations we have seen that the normal potential of the system rises with increasing acidity, the change being quite remarkable in the begining but becoming very slow and remaining almost constant at higher concentrations(greater than 1.5 N) It was therefore, deemed

necessary to investigate fully the influence of hydrogen ions and anions of various acids. To meet this end, potential values in presence of alkali salts of the anions of the acids were also determined. In view of the fact that the value of E_j is directly proportional to the potential observed at the electrode, given the concentration of the solution is kept constant, values of E_j have been given in the majority of cases. E_j has been calculated only when needed.

The following experimental procedure was adopted. In the light cell with a smooth platinum electrode in conjunction with saturated calomel electrode was used for all the measurements. The concentration of chromous chloride(and the chromic-chromous ratio) was maintained constant and the acid(or salt) concentration was changed by mixing the solution and air free distilled water in appropriate proportions. 15 c.c. of chromous chloride solution was taken in the cell(after complete displacement of air by nitrogen) and the total volume made upto 30 c.c. with 3.0 N HCl and water. The e.m.f. was noted in each case when constancy was obtained (in thirty to 45 minutes). The readings are tabulated as follows:

T A B L E XIX.

Changes in e.m.f. with HCl concentrations.

Strength of chromous chloride solution(original)	= 0.0850 N
Concentration of total chromium	= 0.0838 N
Volume of chromous chloride used in each case	= 15.0 c.c.
Total volume made up	= 30.0 c.c.
Concentration of Cr(II)	= 0.1773 N
Ratio Cr(III)/Cr(II)	= 0.0303
Potential of s.c.e.(at 25°C)	= 0.2415 V.

Contd.

Vol. of HCl(3 N)	Vol. of water	Conc. of HCl	Pot. vs. s.c.e.	Electrode potential	p_H
0.0 c.c.	15.0 c.c.	0.00 N	0.5600	0.3185	3.10
0.5 "	14.5 "	0.05 N	0.5815	0.3395	2.15
1.0 "	14.0 "	0.10 N	0.5935	0.3520	1.80
2.0 "	13.0 "	0.20 N	0.6115	0.3700	1.40
5.0 "	10.0 "	0.50 N	0.6405	0.3990	0.75
8.0 "	7.0 "	0.80 N	0.6490	0.4075	0.25
10.0 "	5.0 "	1.00 N	0.6545	0.4125	0.10
12.0 "	3.0 "	1.20 N	0.6565	0.4150	0.05
15.0 "	-	1.50 N	0.6600	0.4185	0.00

(The solutions became green in colour at the end of the experiment)

E_o value calculated for solution without HCl = 0.2567 V.

E_o calculated inpresence of 1.5 N (15 c.c. 3 N HCl) in a total volume of 30 c.c.) HCl = 0.3567 V.

T A B L E XX.

Change inpotential with KCl concentration:

Strength of chromous chloride solution (original) = 0.3550 M

Concentration of total chromium = 0.3868 M

Vollume of $CrCl_2$ used for each experiment = 15.0 c.c.

Total volume made up = 30.0 c.c.

concentration of Cr(ii) in the solution = 0.1775 M

Ratio Cr(iii)/Cr(ii) = 0.0896

Vol. of KCl(3 N)	Vol. of water	Conc. of KCl	Pot vs. s-c-e-	Electrode potential	p_H
-	15.0 c.c.	-	0.5590	0.3175	3.15
0.5 c.c.	14.5 "	0.05 N	0.5690	0.3275	"
1.0 "	14.0 "	0.10 N	0.5760	0.3345	"
2.0 "	13.0 "	0.20 N	0.5845	0.3430	3.10
5.0 "	10.0 "	0.50 N	0.5990	0.3575	"
8.0 "	7,0 "	0.80 N	0.6065	0.3650	"
10.0 "	5.0 "	1.00 N	0.6100	0.3685	"
12.0 "	3.0 "	1.20 N	0.6120	0.3705	"
15.0 "	-	1.50 N	0.6130	0.3715	"

(The solutions became violet in colour at the end of the experiment)

E_o calculated for solution without KCl = 0.2557 V.

E_o calculated in presence of 1.5 N KCl = 0.3097 V.

Inference:

(1). Both HCl and KCl markedly influence the potential value; the maximum potential attained in presence of 1.5 N HCl and KCl respectively are 0.3567Vand 0.3097Vr(In neutral solution the potential is equal to 0.2567 volt)

(2). The maximum increase in E in presence of Hcl =0.1 Volt and inpresence of KCl = 0.054 volt.

(3). Potassium ions in the case of KCl do not influence the potential sinee similar results were obtained with NaCl.

Summary of the tables 19 & 20.

T A B L E XXI.

No.	Conc. of HCl or KCl	Pot. in presence of HCl	Pot. in presence of KCl	Pot.corrected for H alone	p_H
1	-	0.3185	0.3175	0.3180 (average)	3.10
2	0.05 N	0.3395	0.3275	0.3295	2.15
3	0.10 N	0.3520	0.3345	0.3350	1.80
4	0.20 N	0.3695	0.3430	0.3440	1.40
5	0.50 N	0.3990	0.3575	0.3590	1.75
6	0.80 N	0.4075	0.3650	0.3600	0.25
7	1.0 N	0.4125	0.3685	0.3615	0.10
8	1.20 N	0.4150	0.3705	0.3620	0.05
9	1.50 N	0.4185	0.3715	0.3645	0.00

The correction was made by subtracting the change in potential due to KCl from the values obtained for HCl e.g. change in potential due to 0.05 N KCl is equal to 0.3275-0.3175= 0.01 V. Hence net change in potentialduc to hydrogen ion alone(0.05 N HCl) is equal to 0.3395-0.01=0.3295.

In support of the above observations it was thought worthwhile to carryout a similar set of experiments with chromous sulphate in presence of sulphuric acid and sodium sulphate. A neutral solution of chromous sulphate was prepared exactly in a similar

way as chromous chloride by dissolving the pure acid free chromous acetate in 0.1 N sulphuric acid, precipitating the sulphate by alcohol and dissolving in air free water. 3 N solutions of sodium sulphate and sulphuric acid were also prepared from A.R. samples of the reagents. Chromous sulphate was standardised by the same method as chromous chloride, and also the total chromium was estimated .

Determination of Cr(iii)/Cr(ii) in $CrSO_4$ solution:

Vol. of chromous sulphate used	= 2.0 c.c.
Vol. of potassium permanganate taken	= 10.0 c.c.
Strength of permanganate solution	= 0.095 N
Vol. of ferrous ammonium sulphate required for the reduction of unused permanganate	= 4.45 c.c.
Vol. of ferrous solution equivalent to 2 c.c. of permanganate(potentiometrically determined)	=2.1 c.c.
Vol. of ferrous solution equivalent to 2 c.c. of chromous sulphate	= 6.15 c.c.
Strength of chromous sulphate solution	= 0.2783 N.

Estimation of total chromium:

Vol. of the solution used	= 2.0 c.c.
Vol. of ferrous solution required to reduce the dichromate formed (from titration curve)	= 20.1 c.c.
Strength of chromium in mole/litre	= 0.3028 M

Ratio Cr(iii)/Cr(ii):

Concentration of Cr(iii) in the solution	= 0.0245 M
Hence ratio Cr(iii)/Cr(ii)	= 0.095

TABLE XXII.

Changes in e.m.f. of $CrSO_4$ solution with H_2SO_4 concentration:

Strength of the original solution	= 0.2783 M
Concentration of total chromium	= 0.3028 M
Vol. of chromous solution used in each case	= 15.0 c.c.
Total vol. made up	= 30.0 c.c.

contd.

Concentration of Cr(ii) in the cell = 0.1392 M

Ratio Cr(iii)/Cr(ii) = 0.095

Potential of s.c.e. at 25°C = -0.2415

Vol. of 3 N H_2SO_4	Vol. of water	Conc. of H_2SO_4	Pot. vs. s.c.e.	Electrode potential	p_H
-	15.0 c.c.	-	0.5540	0.3125	3.30
0.5 c.c	14.5 "	0.05 N	0.5650	0.3235	2.65
1.0 "	14.0 "	0.10 N	0.5815	0.3400	2.30
2.0 "	13.0 "	0.20 N	0.5930	0.3515	1.90
5.0 "	10.0 "	0.50 N	0.6125	0.3710	1.25
8.0 "	7.0 "	0.80 N	0.6225	0.3810	0.65
10.0 "	5.0 "	1.00 N	0.6260	0.3845	0.50
12.0 "	3.0 "	1.20 N	0.6295	0.3880	0.40
15.0 "	- "	1.50 N	0.6310	0.3895	0.30

(The colour of the solution turned green at the end of the experiment of exposure to air)

E_o calculated in the case of 'neutral' solution = 0.2522 V.

E_o calculated in presence of 1.5 N H_2SO_4 = 0.3292 V.

TABLE XXIII.

Changes in e.m.f. in presence of Na_2SO_4:

Strength of chromous sulphate solution(original) = 0.2733 M

Concentration of total chromium = 0.3028 M

Vol. of chromous sulphate used in each case = 15.0 c.c.

Total volume made up = 30.0 c.c.

Concentration of Cr(ii) in the cell = 0.1392 M

Ratio Cr(iii)/Cr(ii) = 0.0950

Potential of s.c.e. at 25°C = -0.2415 V.

Vol. of Na_2SO_4(3N)	Vol. of water	Conc. of Na_2SO_4	Potential Vs s.c.e.	Electrode potential
-	15.0 c.c.	-	0.5535	0.3120
0.5 c.c.	14.5 "	0.05 N	0.5570	0.3155
1.0 "	14.0 "	0.10 N	0.5615	0.3200
2.0 "	13.0 "	0.20 N	0.5700	0.3285
5.0 "	10.0 "	0.50 N	0.5830	0.3415
8.0 "	7.0 "	0.80 N	0.5890	0.3475
10.0 "	5.0 "	1.00 N	0.5915	0.3500
12.0 "	3.0 "	1.20 N	0.5940	0.3525
15.0 "	- "	1.50 N	0.5945	0.3530

(The solution turned violet in colour at the end of the expt.)

E_o calculated in the case of 'neutral' solution = 0.2517 V.

E_o calculated inpresence of 1.5 N Na_2SO_4 = 0.2927

Inference from tables 22 & 23:

The influence of hydrogen ions on the potential of the chromous sulphate solution was computed from the tables 22 & 23 as is summarised in the following table:

TABLE XXIV.

No.	Conc. of H_2SO_4 or Na_2SO_4	Pot. in presence H_2SO_4	Pot. in presence Na_2SO_4	Pot. corrected for H^+ alone	p_H (table 22)
1.	-	0.3125	0.3120	0.3123	3.30
2.	0.05 N	0.3235	0.3155	0.3200	2.65
3.	0.10 N	0.3400	0.3200	0.3320	2.30
4.	0.20 N	0.3515	0.3350	0.3350	1.90
5.	0.50 N	0.3710	0.3415	0.3415	1.25
6.	0.80 N	0.3310	0.3475	0.3455	0.65
7.	1.00 N	0.3845	0.3500	0.3465	0.50
8.	1.20 N	0.3880	0.3525	0.3475	0.40
9.	1.50 N	0.3895	0.3530	0.3485	0.30

It is seen(from tables 21 and 24) that with sulphuric acid of the same strength as hydrochloric acid the effect on the potential is comparatively less. It is also evident that hydrogen ion concentration has got a definite influence on the electrode potential of the system.

With a view to make a more critical study of this phenomenon , experiments were performed over a wide range of p_H. measurements were made both by decreasing the p_H of the solution to more by the addition of increasing amounts of HCl, as well as by increasing the p_H by the addition of sodium hydroxide solution up to the stage where the precipitation of the hydroxide took place. The concen-tration of Cr(ii) as well as the Cr(iii)/ Cr(ii) ratio were maintained constant in every case by using the same amount(10 c.c.) of chromous chloride solution and keeping the total volume(20 c.c.) constant by the addition of air free water. The readings are tabulated in the following page.

T AB LE XXV.

Changes in e.m.f. under varying H ion concentrations:

Strength of chromous chloride solution	= 0.3550 M.
Concentration of total chromium	= 0.3868 M.
Volume of chromous schloride used in eaxh case	= 10.0 c.c.
Total volume made up	= 20.0 c.c.
Concentration Cr(ii) in the coll	= 0.1775 M
Ratio Cr(iii)/Cr(ii)	= 0.0896
Strength of HCl used	= 3.0 N
Strength of NaOH used	= 1.0 N
Temperature of the experiment	= 25°C

Vol. of HCl/NaOH	Vol. of water	e.m.f. vs. s.c.e.	Electrode potential	p_H
Readings with HCl.				
10.0c.c.	-	0.6610	0.4195	0.0
8.0 "	2.0 c.c.	0.6600	0.4185	0.05
6.0 "	4.0 "	0.6595	0.4180	0.15
4.0 "	6.0 "	0.6590	0.4175	0.35
3.0 "	7.0 "	0.6535	0.4120	0.78
2.0 "	8.0 "	0.6460	0.3985	1.20
1.0 "	9.0 "	0.6345	0.3529	1.80
0.5 "	9.5 "	0.6150	0.3395	2.30
-	10.0 "	0.5590	0.3175	3.15
Readings with NaOH.				
0.5c.c.	9.5 c.c.	0.5900	0.3485	3.60
1.0 "	9.0 "	0.6175	0.3760	3.95
1.5 "	8.5 "	0.6230	0.3815	4.1
2.0 "	8.0 "	0.6260	0.3835	4.25
2.5 "	7.5 "	0.6260	0.3845	4.35(ppt. formed & disappeared)
3.0 "	7.0 "	0.6280	0.3865	4.5(gelatinous ppt. formed)
4.0 "	6.0 "	0.6340	0.3925	4.65(bulky ppt

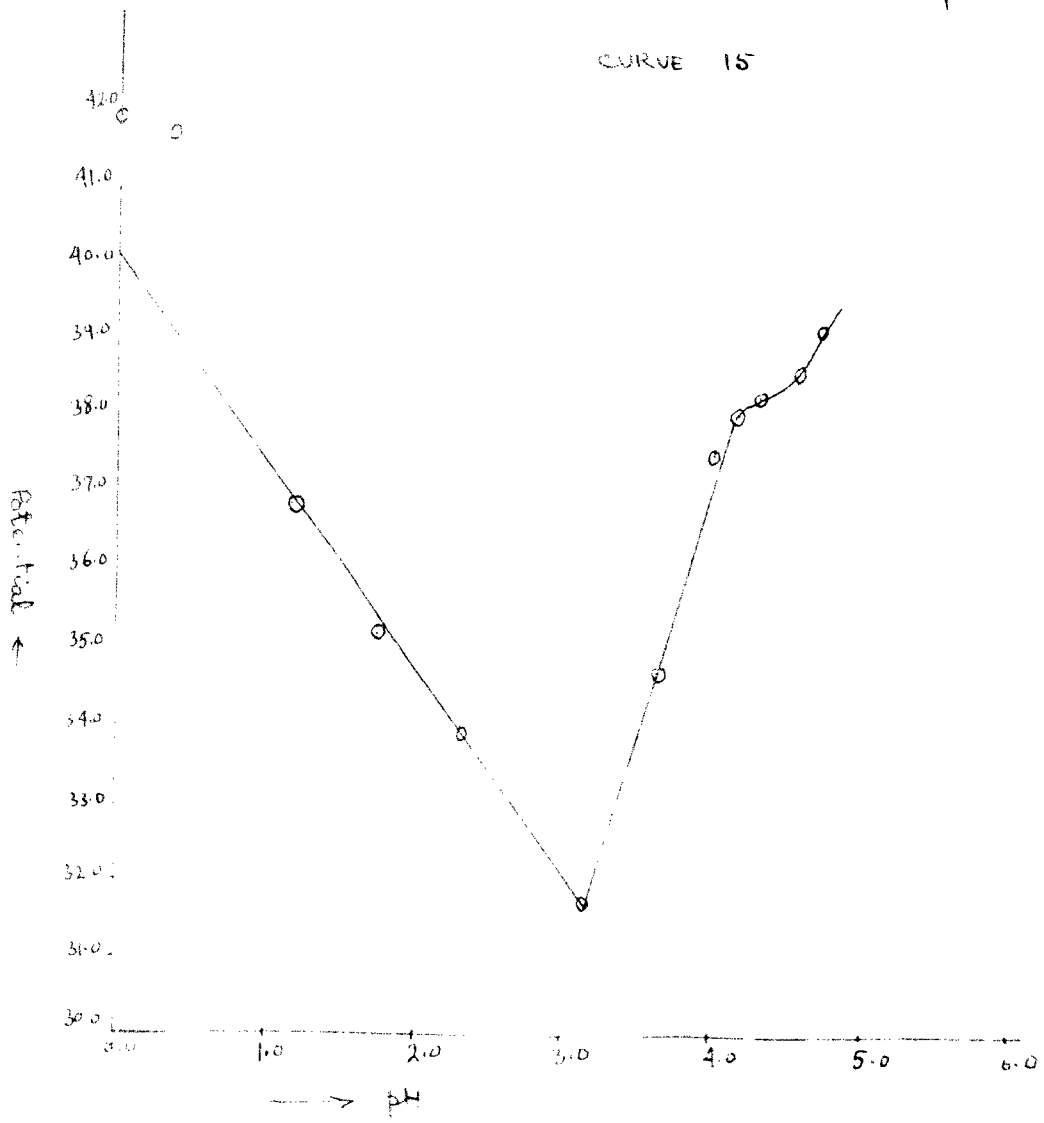
Inference:

(1). The 'neutral' solution with a p_H 3.15 has got the minimum potential (0.3175 V.)

(2). The potential rises both by increasing the p_H(on the addition of alkali) and decreasing the p_H (on the addition of acid)' the

CHANGES IN POTENTIAL WITH VARIATION IN pH

CURVE 15



readings being o.4195 at zero p_H and 0.3835 V. at a p_H of 4.25.

(3). When the p_H exceeds 4.35 by the addition of alkali, the precipitation of the hydrous chromic oxides sets in.

(4). The rise in potential becomes rapid by the addition of alkali after the precipitation p_H (4.35).

(5). The value attains almost a constancy when the p_H reaches zero and further addition of acid has no effect on the e.m.f. of the system.

(6). On plotting a curve (No.15) between the electrode potential and p_H , it was observed that the potential varies with p_H and has got the minimum value with the 'neutral' solution, (p_H 3.15).

INFLUENCE OF ADDITION OF GREEN AND VIOLET VARIETIES OF CHROMIC CHLORIDE ON THE REDOX POTENTIAL OF THE SYSTEM.

Before concluding my investigations on the various aspects of chromous-chromic electrode potential it will be intresting to point out the behaviour of chromous chloride solution on keeping. It was observed that the 'neutral' chromous chloride solution became turbid and violet in colour on keeping in contact with the electrodes, while the same solution changed green in acid medium under similar conditions. Hence it was considered worthwhile to study the variations in potential of the chromous chloride solution by the addition of freshly prepared green and violet samples of chromic chloride solution.

The violet sample of chromic chloride was prepared by the method recommended by WERNER and GUBSER[11]. 50 gms of the pure dark green hydrate was dissolved in 100 c.c. of distilled water in a 250 c.c. F.B. flask and the solution was boiled for an

hour. It was then cooled to 0°C in an ice bath and saturated with hydrogen chloride when violet crystals seperated . This was filtered in a sintered glass funnel and washed with 25 c.c. of fuming hydrochloric acid and then with acetone which removed the unchanged green chloride. It was then dried in a vacuum desiccator and kept in an air tight bottle.

26.44 gms. of this salt was dissolved in air free distilled water and made upto 100 c.c. The strength of the solution was checked by oxidising a known volume (1.0 c.c.) of it to chromate and estimating the latter volumetrically in acid medium. Curiously enough, the solution thus prepared by dissolving the solid hydrate was found to be more transparent than the violet sample obtained on the oxidation of chromous chloride solution.

An exactly 1.00 M solution of the dark green hydrate was also prepared as above.

Variation in potential of chromous chloride solution by the addition of green and violet chromic chloride.

Chromous chloride solution from the storage flask and different amounts of chromic chloride were mixed in the air tight cell after complete displacement of air by nitrogen. 10 c.c. of chromous chloride was always used and the composition (chromic-chromous ratio) varied by taking different amounts of chromic chloride solution and water. The e.m.f. was read with time till constancy was attained. The p_H of the solutions were also noted at the end of each experiment.

TABLE XXVI.

Temperature of the experiment = 25° C.

Value for s.c.c. = +0.2415 V.

Set No.	Time	Potential Vs.s.c.c.	Electrode potential
1. Original chromous solution.			
10 cc. $CrCl_2$ +	5 mints.	0.5375	0.3230
10 c.c. water	10 "	0.5710	0.3295
P_H = 3.1	30 "	0.5710	
	1 Hour	0.5705	
2. Readings with violet sample.			
10 cc. $CrCl_2$,	5 mints	0.5380	0.3235
0.11 cc. $CrCl_3$,	10 "	0.5355	
0.89 cc. water.	30 "	0.5340	0.3225
P_H = 3.1	1 Hour	0.5335	
	5 mints	0.5375	0.3230
10 cc. $CrCl_2$,	10 "	0.5335	
0.33 cc. $CrCl_3$,	30 "	0.5320	0.3115
0.67 cc. water	45 "	0.5335	
P_H = 3.15	1 Hour	0.5325	
4. 10 cc. $CrCl_2$,	5 mints	0.5350	0.3205
1.0 cc. $CrCl_3$,	10 "	0.5310	
9.0 cc. water	30 "	0.5295	0.3180
P_H = 3.15	45 "	0.5295	
	1 Hour	0.5295	
5. 10 cc. $CrCl_2$,	5 mints	0.5200	0.2785
3 cc. $CrCl_3$,	10 "	0.5030	
7 cc. water	30 "	0.5050	0.2340
P_H = 3.2	45 "	0.5055	
	1 Hour	0.5055	
6. 10 cc. $CrCl_2$,	5 mints	0.4900	0.2475
2 cc. $CrCl_3$,	10 "	0.4845	
3 cc. water.	30 "	0.4835	
P_H = 3.25	45 "	0.4830	0.2415
	1 Hour	0.4830	
7. Reading with violet sample.			
10 cc. $CrCl_2$,	5 mints	0.5200	0.2785
0.11 cc. $CrCl_3$,	10 "	0.5155	
0.89 cc. water	30 "	0.5140	0.2625
P_H = 3.15	45 "	0.5130	
	1 Hour	0.5135	

Contd.

Set No	Time	Potential vs.s.c.e.	Electrode potential
8. 10 cc $CrCl_2$, 0.33 cc. $CrCl_3$, 9.67 cc. water p_H =3.15	5 mints	0.5680	0.3265
	10 "	0.5525	
	30 "	0.5500	
	45 "	0.5480	0.3065
	1 Hour	0.5485	
9. 10 cc. $CrCl_2$, 1.0 cc. $CrCl_3$, 9 cc. Water p_H = 3.2	5 mits	0.5450	0.3035
	10 "	0.5335	
	30 "	0.5290	
	45 "	0.5250	
	1 Hour	0.5235	0.2820
	2 Hours	0.5230	
10. 10 cc. $CrCl_2$, 3 cc. $Cr Cl_3$, 7 cc. water p_H = 3.25	5 mints	0.5300	0.2885
	10 "	0.5210	
	30 "	0.5105	
	45 "	0.4980	
	1 Hour	0.4945	0.2530
	2 Hours	0.4940	
11. 10 cc. $CrCl_2$ 9.0 cc. $CrCl_3$, 1.0 cc water. p_H = 3.25	5 mints	0.5030	0.2615
	10 "	0.4900	
	30 "	0.4825	
	45 "	0.4780	
	1 Hour	0.4745	
	2 Hours	0.4730	0.2315

The following table gives the summary of the above sets of reading. The steady value attained in each case was taken for the calculation of the normal potential. The chromous concentration was calculated from the original strength of the sample and Cr(iii) by computing the amount of chromic chloride added with that originally present in the chromous solution.

TABLE XXXII.

Summary of table 23 and E_0 values calculated:

Strength of chromous chloride solution used = 0.9650 N

Ratio Cr(iii)/Cr(ii) = 0.0393

Volume of chromous chloride used in each case = 10.0 c.c.

Set No.	Conc of Cr(ii)	Conc. of Cr(iii)	Log $\frac{Cr(iii)}{Cr(ii)}$	Pot. vs. s.c.e.	Elec. Pot.	E_0
Original solution:						
1.	0.1775 N	0.0159 N	-1.0487	0.5710	0.3295	0.2371
Readings with violet sample:						
2.	0.1775 N	0.0408 N	-0.6333	0.5540	0.3225	0.2702
3.	"	0.0485 N	-0.5703	0.5530	0.3115	0.2618
4.	"	0.0818 N	-0.3334	0.5295	0.2880	0.2681
5.	"	0.1783 N	0.1204	0.5050	0.2640	0.2711
6.	"	0.4818 N	0.3354	0.4830	0.2415	0.2732
Readings with green sample:						
7.	0.1776 N	0.0403 N	-0.6330	0.5590	0. 3175	0.2652
8.	"	0.0485 N	-0.5709	0.5480	0. 2965	0.2638
9.	"	0.0836 N	-0.3334	0.5235	0. 2720	0.2631
10.	"	0.1783 N	0.1204	0.4945	0. 2430	0.2601
11.	"	0.4818 N	0.3354	0.4730	0. 2215	0.2632

E_0 calculated from original solution = 0.2371 V.

E_0 calculated from mixtures of chromous chloride and violet solution of $CrCl_3$ (average value) = 0.2681 V.

E_0 calculated from mixtures of chromous chloride and green solution of $CrCl_3$ (average value) = 0.2631 V.

Inference:

(1). The variation in potential with time is less in the case where violet solutions are added (Set Nos. 2 to 6) than with green solutions.

(2). The time taken for the attainment of constancy is greater in the case of green solutions than with violet samples.

(3). There is very little difference in E_0 values calculated from the three sets of readings.

(4). The value is highest (0.2702) when calculated from the readings obtained by the addition of violet sample of Cr(iii), and the value is lowest (0.2371) with pure chromous.

(5). In every case the solutions became violet towards the end of the experiment.

Influence of some salts and complexing agents of the potential of chromous-chromic system

Molar solutions of the reagents were prepared by dissolving the calculated amount in air free distilled water. 15.0 c.c. of the solution was taken in the cell and nitrogen was passed through for half an hour. The electrodes(a smooth platinum wire indicator electrode and a saturated calomel reference electrode) were then dipped and the solution was covered with a layer of kerosene. 15 c.c. of chromous chloride solution was then transferred into the cell from the storage flask, keeping the elongated delivery tip (described elsewhere) under the kerosine layer, and thoroughly mixed by bubbling nitrogen (a slow current of nitrogen was maintained throughout the experiment). With aview to study the time taken for the attainment of equilibrium in each case and the stability of the complex formed, if any, the changes in potential with time were noted till almost a constancy was attained. The p_H of the mixture was also noted in each case at the end of the experiment.

A fresh smple of the 'neutral' solution of chromous chloride was prepared and the strength of Cr(ii) and the chromic-chromous ratio determined. It was found to be Cr(iii)/Cr(ii) = = 0.118 and Cr(ii) = 0.2873 N.

The readings taken with various reagents are tabulated below:

TABLE XXVII (A).

Volume of chromous chloride solution taken in each case = 15.0 c.c.

Strength of chromous chloride = 0.2873 N

Total volume made up by the addition of

the reagents in each case = 30.0 c.c.

Concentration of Cr(ii) in the cell = 0.1437 N.

Ratio Cr(iii)/Cr(ii) (Original) = 0.1180.

Temperature of the experiment = 24° C.

Potential of S.C.E. = -0.2415 V.

Concentration of the reagent in each case = 1.0 N.

	1. Acetic acid		2. Sodium acetate	
Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 MINTS.	0.4100	0.1685	0.4215	0.1800
10 "	0.4965	0.2550	0.4100	0.1685
20 "	0.5100	0.2685	0.3900	0.1485
30 "	0.5115	0.2700	0.3655	0.1240
45 "	0.5110	0.2695	0.3650	0.1235
60 "	0.5110	0.2695	0.3650	0.1235
90 "	0.5105	0.2690	0.3640	0.1245
p_H	1.95		6.22	
Remarks	Blue solution turned to bluish green.		Seperation of red precipitate. Supernatant liquid turned greenish voilet	

	3. Oxalic acid		4. Potassium Oxalate	
Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.3820	0.1405	0.3900	0.1485
10 "	0.3515	0.1100	0.3510	0.1095
20 "	0.3200	0.0785	0.3135	0.0720
30 "	0.2625	0.0210	0.2830	0.0415
45 "	0.2620	0.0205	0.2500	0.0085
60 "	0.2615	0.0200	0.2425	0.0010
90 "	0.2615	0.0200	0.2425	0.0010
p_H	1.98		6.36	
Remarks	Solution turned redish violet.		Solution turned redish violet(deeper than in 3)	

5. Tartaric acid			6. Potassium Tartarate	
Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.4015	0.1600	0.3935	0.1510
10 "	0.4190	0.1775	0.4010	0.1595
20 "	0.4215	0.18300	0.3820	0.1405
30 "	0.4220	0.1805	0.3565	0.1150
45 "	0.4220	0.1805	0.3435	0.1020
60 "	0.4215	0.1800	0.3430	0.1015
90 "	0.4210	0.1795	0.3420	0.1005
p_H	1.68		3.95	
Remarks	Solution turned reddish violet		Slow seperation of white needle shaped crystals. Supernatant liquid turned dark green.	

7. Citric acid			8. Sodium citrate	
Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.4355	0.1940	0.3180	0.0765
10 "	0.4220	0.1805	0.3015	0.0600
20 "	0.4220	0.1805	0.2925	0.0510
30 "	0.4210	0.1795	0.2930	0.0515
45 "	0.4195	0.1780	0.2935	0.0520
60 "	0.4195	0.1780	0.2945	0.0530
90 "	0.4180	0.1765	0.2950	0.0535
p_H	1.98		4.12	
Remarks	Solution remained reddish violet; no change on exposure to air		Solution remained reddis violet.	

9. Potassium Molybdate			10. Sodium Tugstate	
Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.2900	0.0585	0.6815	0.4400
10 "	0.2625	0.0210	0.7330	0.4915
20 "	0.2480	0.0065	0.7845	0.5430
30 "	0.2400	-0.0015	0.7930	0.5515
45 "	0.2385	-0.0030	0.7985	0.5570
60 "	0.2380	-0.0035	0.7990	0.5575
90 "	0.2370	-0.0045	0.8000	0.5585
p_H	8.46		9.44	

11. Trisodium phosphate

12 Sodium biphosphate

Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.3200	0.0785	0.3875	0.1460
10 "	0.3315	0.0900	0.3950	0.1535
20 "	0.3390	0.0975	0.3990	0.1575
30 "	0.3425	0.1010	0.4010	0.1595
45 "	0.3430	0.1015	0.4015	0.1600
60 "	0.3440	0.1025	0.4025	0.1610
90 "	0.3445	0.1030	0.4030	0.1615
p_H	3.85		3.36	
Remarks	Grey precipitate; supernatant liquid turns dark green		Greyish white precipitate turning dark green; supernatant liquid also green.	

13. Pyridine

14. Sodium carbonate

Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.4925	0.2510	0.3880	0.1465
10 "	0.5130	0.2715	0.4100	0.1685
20 "	0.5400	0.2985	0.4215	0.1800
30 "	0.5535	0.3120	0.4220	0.1805
45 "	0.5545	0.3130	0.4230	0.1815
60 "	0.5540	0.3125	0.4210	0.1795
90 "	0.5540	0.3125	0.4200	0.1785
p_H	7.54		10.40	
Remarks	Gradual seperation of red precipitate; supernatant liquid slowly turns greenish violet.		Red crystalline precipitate; slow seperation of violet hydroxide; supernatant liquid becomes colourless.	

15. Ammonium chloride

16. Ammonium hydroxide

Time	Potential Vs. s.c.e.	Electrode potential	Potential Vs. s.c.e.	Electrode potential
5 Mints	0.4165	0.1750	0.6925	0.4510
10 "	0.5210	0.2795	0.7130	0.2715
20 "	0.5980	0.3565	0.7185	0.4770
30 "	0.6300	0.3885	0.7210	0.4795
45 "	0.6295	0.3880	0.7210	0.4795
60 "	0.6280	00.3865	0.7215	0.4800
90 "	0.6275	0.3860	0,7225	0.4810
p_H	3.10		10.04	
Remarks	Blue solution turning bluish violet.		Bluish grey precipitate turning slightly reddish; supernatant liquid gradually turns violet	

Experiments were also carried out with 'neutral' solution and in presence of HCl, H_2SO_4, KCl, and K_2SO_4 using the same sample of chromous chloride and under identical conditions. The readings are summarised in the following table:

TABLE XXVII (B).

S.No.	Reagent used	Potential	p_H	Remarks
1.	Acetic acid	0.2695	1.95	Blue solution turning violet.
2.	Sodium Acetate	0.1235	6.22	Red crystals of chromous acetate; supernatant liquid turns greenish violet
3.	Oxalic acid	0.020	1.98	Reddish violet solution
4.	Potassium Oxalate	0.001	6.36	Dark solution with reddish violet tinge.
5.	Tartaric acid	0.1805	1.68	Reddish violet solution.
6.	Potassium Tartarate	No steady value	3.95	Slow seperation of white needle shaped crystals; supernatant liquid turns dark green.
7.	Citric acid	0.1780	1.98	Reddish violet solution.
8.	Sodium citrate	No steady value	4.12	Reddish violet solution.
99.	Potassium Molybdate	No steady vale	8.46	Brown yellow precipitate; slow seperation of hydroxide; supernatant liquid turns colourless.
10.	Sodium Tungstate	No steady value	9.44	Greenish grey precipitate; seperation of hydroxide; supernatant remains bluish green.
11.	Trisodium Phosphate	(0.1015)	3.85	Grey precipitate; supernatant liquid turns green.
12.	Sodium biphosphate	(0.161)	3.36	Greyish white precipitate turning dark green; supernatant liquid also turns green.
13.	Pyridine	0.3125	7,54	Gradual seperation of red precipitate; supernatant liquid turns greenish violet

TABLE XXVII(B) Continued

S.No.	Reagent used	Potential	p_H	Remarks
14.	Ammonium chloride	0.3885	3.10	Blue solution turning bluish violet.
15.	Ammonium hydroxide	0.4795	10.04	Bluish grey precipitate and supernatant liquid slowly turns violet.
16.	Sodium carbonate	(0.1795)	10.40	Red crystalline precipitate; slow speration of violet hydroxide; supernatant liwuid turns colourless.
* 17.	Potassium chloride	0.3710	3.10	Solution turns bluish violet.
18.	Hydrochloric acid	0.4035	1.46	Solution turns green.
19.	Sulphuric acid	0.4235	1.65	Solution turns green.
20.	Potassium sulphate	0.3810	3.92	Solution turns green.
21.	(Neutral solution)	0.3230	3.15	Solution turns bluish violet.

* Only the summary of the readings with the following reagents have been given.

Discussion:

The experiments on the potential measurements of chromous chloride solution of varying concentrations in presence of acids and neutral salts and under controlled p_H, using mercury and platinum electrodes have thrown new light on certain aspects of the problem of Cr(ii)-Cr(iii) redox system. The conclusions arrived at are discussed in the following paragraphs.

The solution exhibits a far greater potential stability at the platinum electrode (taking about thirty to forty five minutes for arriving a steady potential) than at mercury electrode(about forty eight hours), although the potential value for the latter is higher ($E = 0.4503$ for $Cr(iii)/Cr(ii) = 0.112$ and E_o calculated $= 0.3948$ than for the former ($E = 0.3218$ and E_o calculated $= 0.2554$ V. for the same ratio. vide page 28). These observations cannot merely be explained by assuming the catalytic oxidation of chromous chloride at the platinum (loc. cit). Some other factors, probably more important, responsible for such a behaviour seem to be (i) the adsorption of chromous ions at the mercury surface—a fact which finds support in my experiments on the potential measurements on stirring the solution, when an instantaneous fall in potential was observed (vide table No. 5 page 29), and (ii) the role of the chloride ions which may be contributing towards the higher potential value but at the same time responsible for the long period required for the attainment of the steady potential for the latter, it may be argued that these ions are slowly reacting with mercury to give mercurous chloride thereby not allowing easily the establishment of equilibrium condition

Further support to the view point that the chloride ions help in raising the potential value is forthcoming from the

experiments on the variation in e.m.f. with time at the two electrodes by the addition of HCl and KCl (vide tables 7 and 8 page 31, 32). From these observations it is evident that both $H^{\cdot}$ and $Cl^{\prime}$ ions make the electrode more positive although to a different extent (Pt—0.321 for 'neutral' solution, 0.4203 in presence of 1.5 N HCl and 0.3718 in presence of 1.5 N KCl; Hg —0.4503 for 'neutral' solution, 0.5113 and 0.5103 in presence of 1.5 N HCl and KCl respectively for the chromic-chromous ration0.112). The striking point, however, is that the potential values for HCl and KCl at the mercury electrode are almost the same. This shows that the chloride ions influence the mercury electrode to such an extent that even the role of hydrogen ions (however small) is over shadowed. The dilution of the solution brings about a decrease in the electrode potential (vide table No 12 page 37), That it is due to catalytic oxidation of chromous ions in presence of water seems improbable since experiments were carried out in an inert atmosphere and all possible precautions were taken to exclude atmospheric osygen. It may be due to the fact that both Cr(ii and Cr(iii) hydroxides are weak bases ($\triangle F$ = -140.5 K cal for $Cr(OH)_2$ and -205.5 K Cal for $Cr(OH)_3$) and undergo hydrolytic dissociation as $Cr^{\cdot\cdot} + 2H_2O \rightleftharpoons Cr(OH)_2 + 2H^{\cdot}$ and $Cr^{\cdot\cdot\cdot} + 3H_2O \rightleftharpoons Cr(OH)_3 + 3H^{\cdot}$. Under these conditions, the removal of Cr(ii) and Cr(iii) would depend upon the extent to which the hydrolysis of both the ions take place (vide infra); and as such, it is bound to influence the chromic-chromous ratio. The explaination would have found further support if the concentration of Cr(iii) could be estimated seperately and not merely by subtracting the value for Cr(ii) from the total chromium concentration.

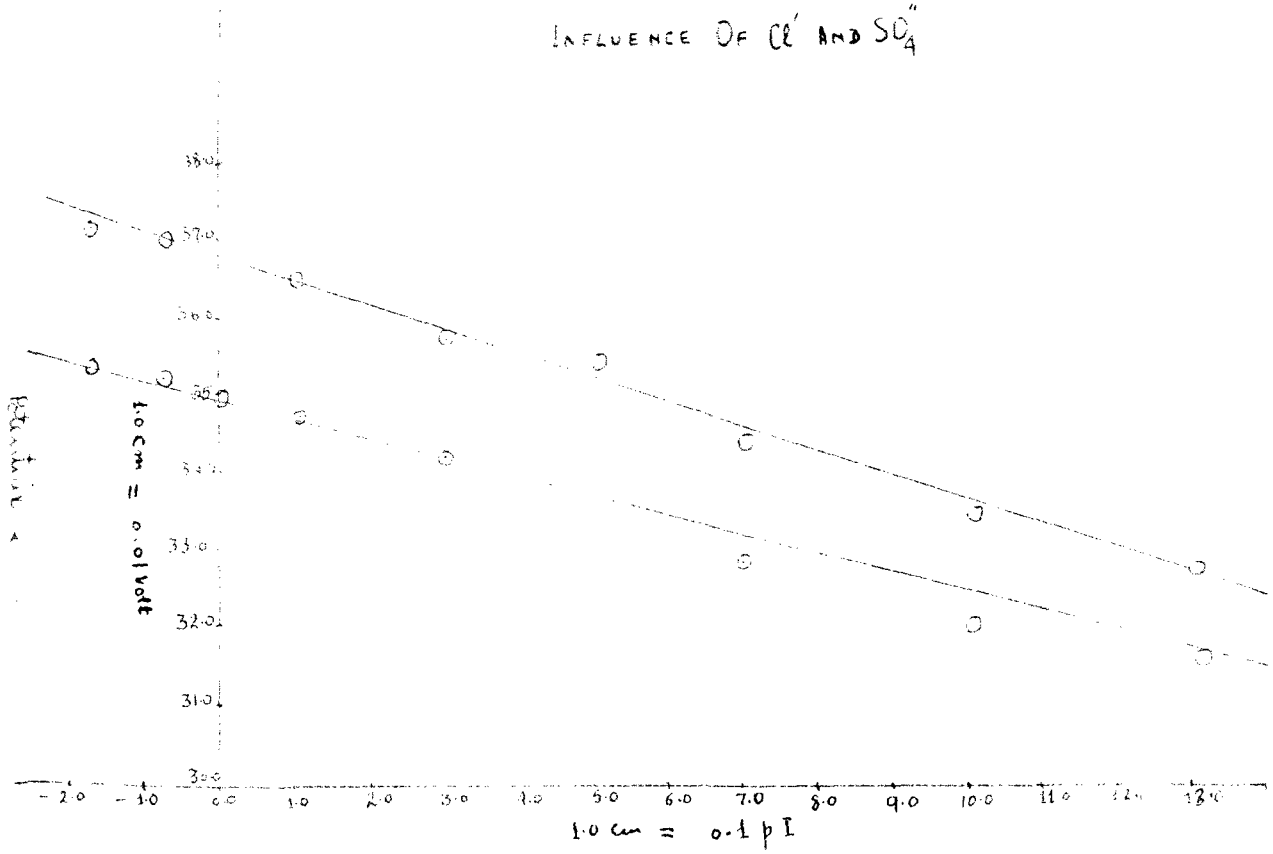
Reference has already been made to the fact that very few data exist for the E_o values of $CrCl_2$-solution prepared by reducing chromic chloride with zinc and hydrochloride acid. Attempt was, therefore, made to determine the E_o value at the platinum electrode (this being chosen for further studies in view of its suitability). The titration method (vide page 41) for the determination of the standard potential gave E_o vale for 'neutral' solution as 0.2684 volt, and 0.2816 V, 0.3628 V and 0.3682 V in presence of 0.05 N, 1.0 N and 2.0 N HCl respectively (vide table No. 17 page 45). On plotting E_o value against the concentration of HCl, a parabolic curve was obtained showing that E_o values show but little change beyond the acid concentration of 1.8 N.(vide curve No.). Useful information about the Cr(ii)-Cr(iii) system was obtained on plotting $\log \frac{ox}{red}$ against electrode potential at various concentrations (vide curve Nos. 10a,b,c) The slope of the lines give the value 0.057 thereby pointing towards the fact that the reaction is a simple one electron reaction. Titrations carried out with H_2O_2 instead of potassium dichromate gave more or less similar results.

Influence of acids and salts on the chromous-chloride system (using platinum electrode:

The intresting observations described in the foregoing paragraphs warranted the necessity of a systematic and detailed study of the potentiometric behaviour of chromous chloride solution. The influence of acids was seen by carrying out measurements with $CrCl_2$ in presence of HCl and HCl and also with $CrSO_4$ in presence of H_2SO_4 and Na_2SO_4 to account seperately for hydrogen ions from the respective acids(vide table Nos. 19-24 page 47-52). It can be seen from these observations that (i) the potential increases with increase in concentration of either HCl or H_2SO_4, the change being more pronounced

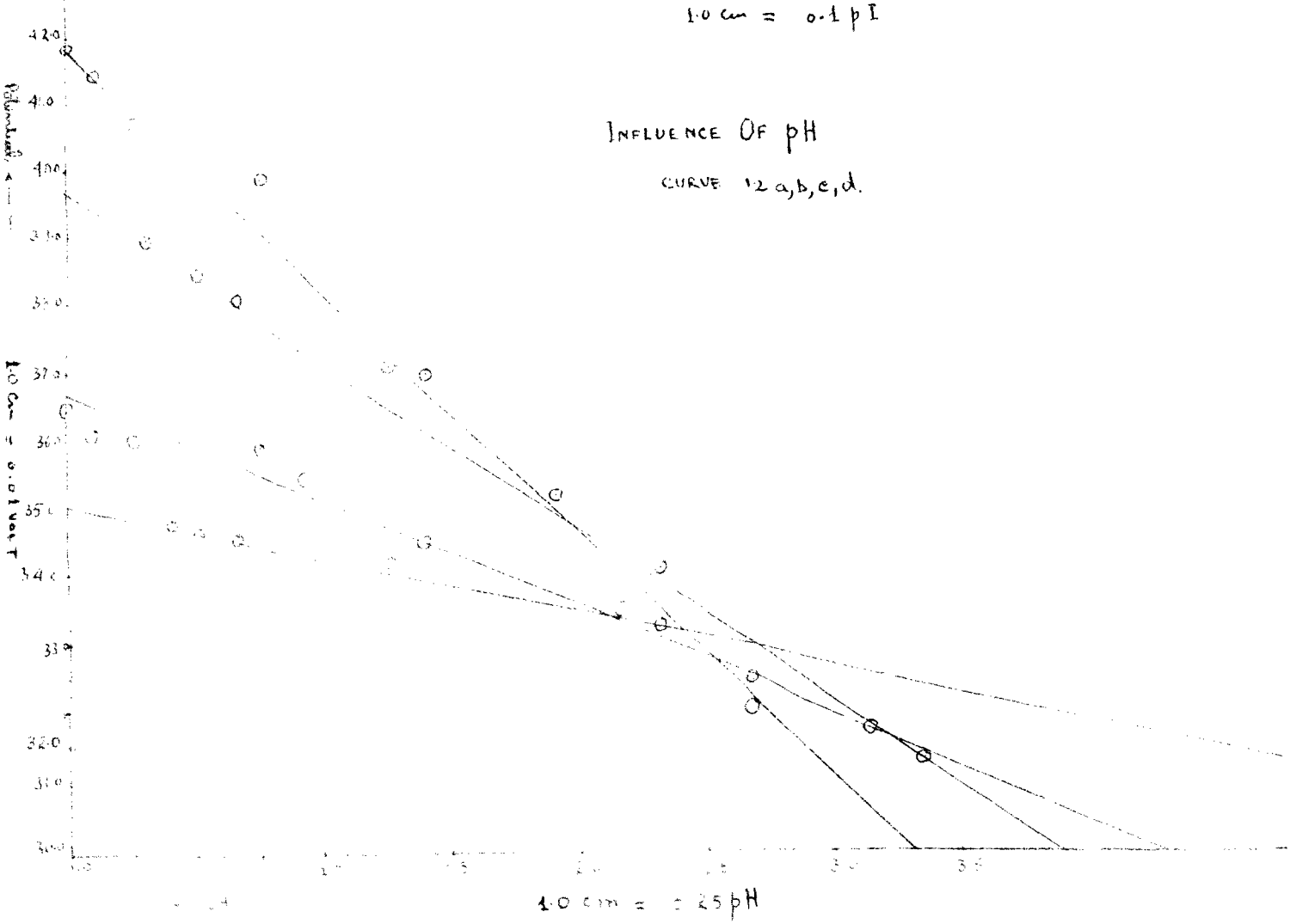
CURVE 13, 14

INFLUENCE OF Cl' AND SO_4''



INFLUENCE OF pH

CURVE 12 a, b, c, d.



with the former, (ii) the chloride ions exert a much greater influence than the sulphate ions.

Theoretical considerations involved in such changes may be seen by drawing curves between p_H (for the two acids) and E on the one hand, and between p_{Cl} and $p_{SO_4^{--}}$ on the other. (vide table Nos. 21 and 24). The curves (Nos. 12 to 14) are all straight lines and from these the values of E_o and the influence of various ions (hydrogen chloride and sulphate) can be determined.

Assuming that the equation $E = E_o - 0.059 \log \frac{Cr(iii)}{Cr(ii)} \times I^n$ (where I stands for the ion concerned) holds good in this case, instead of $E = E_o - 0.059 \log \frac{Cr(iii)}{Cr(ii)}$, then for a constant ratio of Cr(iii)/Cr(ii), in the equation $y = mx + c$, c will be equal to $E_o - 0.059 \log \frac{Cr(iii)}{Cr(ii)}$ and y and m will be equal to E and $-0.059n$ respectively. Also $-\log (I)$ would represent p_H , p_{Cl} or p_{SO_4}. The values of m and c from the curves and the calculated values of n and E_o are given in the following table. E_o values as calculated from potential measurements are also given for comparison.

TABLE XXVII (C)

Electrolyte	m (-ve)	n (-ve)	c	E_o (from curve)	E_o (calculated from potential)
HCl	0.0331	0.61	0.411	0.3553	0.3537
KCl	0.0320	0.520	0.368	0.3032	0.3032
H' (corrected for Cl')	0.0162	0.274	0.334	0.3022	0.3023
H_2SO_4	0.0230	0.440	0.359	0.3307	0.3292
Na_2SO_4	0.0211	0.406	0.348	0.2877	0.2897
H' (corrected for SO_4^{--})	0.0071	0.121	0.353	0.2927	0.2937

From the foregoing table it may be seen that there exists a fairly good agreement between the E_o values for HCl, KCl, $H^{\cdot}$ ion (corrected for $Cl^{\cdot}$) and Na_2SO_4 obtained from the curves and those calculated from the potential values. The values for H_2SO_4 and $H^{\cdot}$ corrected for $SO_4^{''}$ show a little deviation. It may further be seen that the influence of the ions on the observed redox potential is $Cl^{\cdot} > SO_4^{''} > H^{\cdot}$ and the combined influence of $H^{\cdot}$ and $Cl^{\cdot}$ (as observed from HCl is greater than $H^{\cdot}$ and $SO_4^{''}$ (as observed from H_2SO_4). The following relationship for the various ions may now be given:

$$E = E_o - 0.059 \log \frac{[Cr^{+++}]\,[Cl^-]^{-0.520}}{[Cr^{++}]} \qquad \text{(i)}$$

$$E = E_o - 0.059 \log \frac{[Cr^{+++}]\,[SO_4^{--}]^{-0.406}}{[Cr^{++}]} \qquad \text{(ii)}$$

$$E = E_o - 0.059 \log \frac{[Cr^{+++}]\,[H^+]^{-0.274}}{[Cr^{++}]} \qquad \text{(iii)}$$

and in the case of H_2SO_4 ,

$$E = E_o - 0.059 \log \frac{[Cr^{+++}]\,[H^+]^{-0.121}}{[Cr^{++}]} \qquad \text{(iv)}$$

(On the above basis n for HCl and H_2SO_4 should be 0.782 and 0.527 respectively as against 0.610 and 0.440 obtained from the curves).

Influence of $Cl^{\cdot}$ and $SO_4^{''}$ ions:

Assuming that complex ion formation between potassium chloride and chromous and chromic chlorides takes place, the following relationships may be deduced:

$$CrCl_2 + xKCl \rightleftharpoons K_xCrCl_{2+x} \qquad \text{(v)}$$

$$CrCl_3 + yKCl \rightleftharpoons K_yCrCl_{3+y} \qquad \text{(vi)}.$$

If K_1 and K_2 are taken as the complexing constants for the above two equations, then

$$K_1 = \frac{[K_xCrCl_{2+x}]}{[CrCl_2]\,[KCl]^x} = \frac{[CrCl_{2+x}^{-x}]}{[Cr^{++}]\,[Cl^-]^{2+x}}$$

$$\text{and } K_2 = \frac{[K_yCrCl_{3+y}]}{[CrCl_3]\,[KCl]^y} = \frac{[CrCl_{3+y}^{-y}]}{[Cr^{+++}]\,[Cl]^{3+y}}$$

$$Cr^{++} = \frac{1}{K_1} \cdot \frac{[CrCl_{2+x}^{-x}]}{[Cl^-]^{2+x}}$$

$$\text{and } Cr^{+++} = \frac{1}{K_2} \cdot \frac{[CrCl_{3+y}^{-y}]}{[Cl^-]^{3+y}}$$

$$\therefore \frac{Cr^{+++}}{Cr^{++}} = \frac{K_1}{K_2} \cdot \frac{[CrCl_{3+y}^{-y}]}{[CrCl_{2+x}^{-x}]} \cdot \frac{[Cl^-]^{2+x}}{[Cl^-]^{3+y}}$$

$$= \frac{K_1}{K_2} \cdot \frac{[CrCl_{3+y}^{-y}]\,[Cl^-]^{x-y-1}}{[CrCl_{2+x}^{-x}]}$$

Now, the equation $E = E_o - 0.059 \log \frac{Cr^{+++}}{Cr^{++}}$ takes the form

$$E = E_o - 0.059 \log \frac{K_1}{K_2} \cdot \frac{[CrCl_{3+y}^{-y}]\,[Cl^-]^{x-y-1}}{[CrCl_{2+x}^{-x}]}$$

$$= E_o - 0.059 \log \frac{K_1}{K_2} \cdot \frac{[CrCl_{3+y}^{-y}]}{[CrCl_{2+x}^{-x}]} - 0.059 \log [Cl^-]^{x-y-1}$$

From the curve, the value of $n = 0.620$ i.e. $x-y-1 = 0.52$

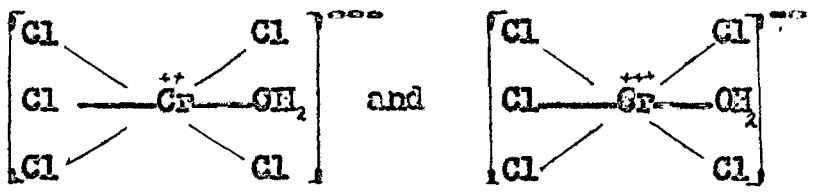
If y is taken as unity, x will be 1.5, i.e. x:y as 3:2.

The probable reactions for the complex formation are:

$$CrCl_2 + 3KCl = K_3CrCl_5$$

and $$CrCl_3 + 2KCl = K_2CrCl_5$$

The complex anions $[CrCl_5]^{---}$ and $[CrCl_5]^{--}$ may be represented as



E.A.N. = 22 + 12 = 34 E.A.N. = 21 + 12 = 33

Although the halide ions often co-ordinate strongly, these may be generally divided into groups, i.e., those of the very stable complexes such as platinum group metals and those relatively labile halide complexes of the type formed by elements of the first transition group (giving positive test for the halide in aqueous solutions). To the latter type belong $K_2CrCl_4.2H_2O$ (X-rays, however, show the existence of copper(II) chloride-2 hydrate admixed with KCl in the crystal lattice[15]). It seems, therefore, quite likely that strong co-valent bounding between the Cr(ii) or Cr(iii) and Cl' ions does not exist and [illegible] these forms an ionic bonding, in view of the almost electronegativity.

The influence of sulphate ions on chromous sulphate solution is also of a similar nature since the sulphate radical is known to occupy co-ordination position (one or two).

The possible reactions may be,

$$2CrSO_4 + xNa_2SO_4 = Na_{2x}Cr_2(SO_4)_{2+x}$$

and $Cr_2(SO_4)_3 + yNa_2SO_4 = Na_{2y}Cr_2(SO_4)_{3+y}$

$$K_1 = \frac{|Na^-|^{2x}|Cr_2(SO_4)^{-x}_{2-x}|}{|Na^-|^{2x}|Cr^{--}|^2|SO_4^{--}|^{2-x}} = \frac{|Cr_2(SO_4)^{-x}_{2-x}|}{|Cr^{--}|^2|SO_4^{--}|^{2-x}}$$

$$\therefore |Cr^{--}| = \sqrt{\frac{|Cr_2(SO_4)^{-x}_{2-x}|}{K_1|SO_4^{--}|^{2-x}}} .$$

Similarly, $K_2 = \frac{|Cr_2(SO_4)^{-y}_{3-y}|}{|Cr^{---}|^2|SO_4^{--}|^{3-y}}$

$$\therefore |Cr| = \sqrt{\frac{|Cr_2(SO_4)^{-y}_{3-y}|}{K_2|SO_4^{--}|^{3-y}}}$$

$$E = E_o - 0.059 \log \sqrt{\frac{K_1}{K_2}} \cdot \sqrt{\frac{|Cr_2(SO_4)^{-y}_{3-y}||SO_4^{--}|^{2-x}}{|Cr_2(SO_4)^{-x}_{2-x}||SO_4^{--}|^{3-y}}}$$

$$= E_o - 0.059 \log \sqrt{\frac{K_1}{K_2}} \cdot \sqrt{\frac{|Cr_2(SO_4)^{-y}_{3-y}|}{|Cr_2(SO_4)_{2-x}|}} - 0.059 \log |SO_4|^{\frac{x-y-1}{2}} .$$

From the curve, the value of $n = -0.4$

$\therefore \frac{x-y-1}{2} = -0.4$; or $x-y = 1-0.8 = 0.2$

If y is taken as unity, then $x = 1.2$

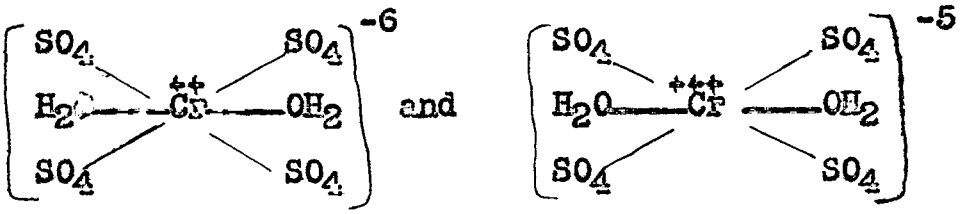
or $x : y = 1.2 : 1 = 6 : 5$.

Hence the above two equations can be written as

$$2CrSO_4 + 6Na_2SO_4 \longrightarrow Na_{12}Cr_2(SO_4)_8 \text{ or } 2Na_6Cr(SO_4)_4 ,$$

and $$Cr_2(SO_4)_3 + 5Na_2SO_4 \longrightarrow Na_{10}Cr_2(SO_4)_8 \text{ or } 2Na_5Cr(SO_4)_4 .$$

The complex anions can be represented as:



E.A.N. = 22 + 12 = 34 E.A.N. = 21 + 12 = 33 .

The formation of such complex anion would involve a one electron transfer reaction which should give an appreciable redox potential. Also again the bonds should not be purely co-valent.

The influence of hydrogen ions on the redox potential appears to be entirely different from that of the anions on chromous chloride and sulphate solutions. It can be seen from the table xxvii(c) that the values of n for HCl and H_2SO_4 are much lower than those obtained by adding up the values for H^+ and Cl^- , and H^+ and SO_4^{--} respectively. It is thus evident that simple relationships such as

$$E_1 = E_0 - 0.059 \log \frac{[Cr^{+++}][H^+]^{n_1}[Cl^-]^{n_2}}{[Cr^{++}]}$$

and $$E_2 = E_0 - 0.059 \log \frac{[Cr^{+++}][H^+]^{n_3}[SO_4^{--}]^{n_4}}{[Cr^{++}]}$$

can not hold good.

The role of hydrogen ions may then be to influence the hydrolytic tendency of the chromic ions. A simple hydrolytic mechanism as

$$CrCl_3 + 3H_2O \rightleftharpoons Cr(OH)_3 + 3HCl$$

and $$CrCl_2 + 2H_2O \rightleftharpoons Cr(OH)_2 + 2HCl$$

however, does not explain the experimental results. Such a mechanism would mean that:

$$K. \frac{[Cr(OH)_3][H^+]}{[Cr(OH)_2]}$$

should be introduced for Cr(iii)/Cr(ii) and for a constant ratio of the two hyderoxide, E should increase with increase in the value of -log [H] i.e. p_H. On the other hand experimental results in this case show an increase in the value of E with an increase in [H] (vide table 17).

Such a behaviour shown by chromous and chromic ions in highly acidic solutions is not surprising in view of the different isomeric forms, their hydrolysability and the difference in the stability of the two hydroxides. For instance according to Lamb and Fonda[13] chromium ions hydrolyse as:

$$\underset{\text{(violet)}}{Cr^{+++}} + H_2O = Cr(OH)^{++} + H^+$$

$$\underset{\text{(green)}}{CrCl_2^+} + H_2O = Cr(OH)^{++} + H^+ + 2Cl^-$$

the green variety $[Cr(H_2O)_4Cl_2]Cl$ being stable in chloride solutions. Again the chromous hydroxide formed by hydrolysis of chromous ions is so unstable inspite of the fact that Hume and Stone[14] reported $K = 1.0 \times 10^{-17}$ for the solubility product, it is rather risky to base conclusions by considering the appreciable ionisation of $Cr(OH)_2$ to give chromous ions under these p_H conditions. It seems quite certain that the effect of H^+ ions is to check hydrolysis, specially that of Cr^{++} ions since these rapidly change to Cr^{+++} ions and should mean removal of a large number of Cr^{++}. It is also clear from the reaction

$$CrCl_2 + H_2O = Cr(OH)^{++} + H^+ + 2Cl$$

that the addition of HCl(i.e. both H⁺and Cl⁻ ions) help in the release of lesser number of Cr(iii) ions in solution(a fact supported by the colour of the solution).

The behaviour of chromous chloride solution with respect to its redox potential changes by increasing the p_H on adding gradually increasing amounts of castic soda, is intresting. After a certain p_H range has been reached the potential increases with increase in p_H vide table 25 and curve No.15). This region falls just before precipitation sets in (p_H range 4.35). It is in this range that the reactions $Cr(OH)_2 = Cr^{++} + 2\,OH^-$; $Cr(OH)_3 = Cr^{+++} + 3OH^-$ take place.

$$K_1 = \frac{[Cr^{++}][OH^-]^2}{[Cr(OH)_2]} = 1.0 \times 10^{-17}$$

$$K_2 = \frac{[Cr^{+++}][OH^-]^3}{'Cr(OH)_3'} = 6.7 \times 10^{-31}$$

$$\therefore \frac{[Cr^{+++}]}{[Cr^{++}]} = \frac{[Cr(OH)_3]}{[Cr(OH)_2]} \times \frac{1}{[OH]} \times 6.7 \times 10^{-14}$$

since $[H^+][OH^-] = 1 \times 10^{-14}$, it follows that,

$$\frac{[Cr^{+++}]}{[Cr^{++}]} = \frac{[Cr(OH)_3]\ [H^+]}{[Cr(OH)_2]} \times 6.7.$$

This would mean an increase in the observed potential (for a constant ratio of Cr(iii)/Cr(ii)) with increase in the p_H value.

A far more intresting behaviour than that found by the gradual addition of increase in amounts of NaOH, is observed when potential are measured in presence of some salts and complexing

agents. The values fall under two categories:

(i). A low p_H range of 1.462 to 6.36: In this range high values are obtained when either the anions form labile(not purely co-valent) complexes or sufficient hydrogen ions are present to check the hydrolytic tendencies of the Cr(ii) and Cr(iii) ions. This holds good even in the case of ammonium chloride. Low values are obtained in presence of acids and salts which form complexes with a very stable ligand e.g. oxalic, citric, and tartaric acids and their salts and sodium phosphate.

(ii) A high p_H range of 7.54 to 10.4: In this range high potential values are obtained with ammonium hydroxide and pyridine. The values attain constancy in spite of the fact that separation of the precipitate takes place. This behaviour is similar to that observed by the addition of NaOH where the potential increased with p_H . It is rather intresting to note that sodium tugstate gives a very high potential value although constancy could not be achieved .

From the above it is seen that no linear relationship between p_H and potential is obtained, in presence of weak acids and their salts. This behaviour is unlike that observed for HCl and H_2SO_4.

In most of these cases it has been found that unlike HCl, KCl, H_2SO_4 and Na_2SO_4, the potential takes a larger time to attain constancy (e.g. a steady value is not attained in the case of tartarate, citrate, molybdate, tungstate and carbonate and even after 1½ hours). Further, instead of the usual rise in potential with time, a fall is observed from the very beginning of the experiment.

The anomalous behaviour in potential changes observed by the addition of green and violet chromic chloride to a chromous solution under equilibrium, could not be explained on this basis and hence polarographic studies were attempted (vide chap 4).

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CHAPTER III

THE INFLUENCE OF THE PRESENCE OF ACIDS, SALTS AND THEIR MIXTURES ON THE UTILITY OF CHROMOUS CHLORIDE AS AN ANALYTICAL REAGENT.

Amongst the earlier workers who used chromous chloride for quantitaive estimation of metal ions, Zintl and Rienacker[1] recommended copper sulphate for the standardisation of the solution. According to them the titration can be carried out successfully by reducing hot copper sulphate solution containin 2 to 20 % hydrochloric acid, and if the solution contains much chloride the reduction is incomplete. However, when dilute acetic acid was used as a medium for titration, presence of chloride ions was found to be desireable.

More recently some work has been done on the estimation of chromous ions by Isao Muraki[2, 3] and Lingane and Miedrach.[4] The latter authors while studying the reduction of +4 and+6 selenium&tellurium with chromous ions, have attempted to find conditions of acidity under which the results were more accurate. Zintl and Schloffer[5] found that the presence of 2 to 15 % sulphuric acid was necessary for the accurate estimation of ferric iron, and also that the presence of hydrochloric acid interfered in the reaction. The estimations were quite unreliable inpresence of more than 10 % HCl. Similarly when chromous sulphate was used by these authors for the estimation of copper in presence of sulphuric acid, the first stage reduction, Cu(ii)- Cu(i), was not predominant. The end point was always determined by the second break when all the Cu(ii) was reduced to metallic copper. For the estimation of mercury(ii) using chromous chloride Zintl and Rienacker[6] found that the presence of 5% HCl was necessary

to give the theoretical results, greater concentration giving higher values. Better results were obtained at higher temperatures. The presence of sulphuric acid in the case of chromous sulphate, and hydrochloric acid or a chloride and acetic acid in the case of chromous chloride were found necesaary for the estimation of silver and gold[7]. Concentrated hydrochloric acid and calcium chloride solution have also been used by several workers[8-11] as media for the estimation of antimony and Molybdenum.

From the above, it is clear that hydrogen and chloride ions have got important role in the use of chromous chloride as an analytical reagent, but no systematic investigation seems to have been made on the actual role of these ions for the use of this reagent in analytical chemistry. This chapter deals with my investigation on the use of chromous chloride in oxidation reduction potentimetric titrations. Copper sulphate as a neutral solution and in presence of HCl, H_2SO_4, HAc , KCl, K_2SO_4, NH_4Cl , $(NH_4)_2SO_4$, NaAc, mixtures of HCl and KCl, H_2SO_4 and K_2SO_4 etc was titrated against chormous chloride. Titrations were also carried out at higher temperatures.

In an oxidation reduction titration in which the valency change is unity, the potential at the equivalence point E_q is given by $E_q = \frac{E_1 + E_2}{2}$ where E_1 and E_2 are the electrode potentials of the system $Ox_1 = Red_1$ and $Ox_2 = Red_2$ respectively. The reduction of copper sulphate by chromous chloride proceeds in two stages.

(a) $Cu(ii) + Cr(ii) = Cu(i) + Cr(iii)$

(b) $Cu(i) + Cr(iii) = Cu + Cr(iii)$

The potentials of the systems involved are:

(i). $Cu(ii) + e = Cu(i)$ $\quad E = -0.153$

(ii). $Cu(i) + e = Cu$ $\quad E = -0.521$

(iii). $Cr(ii) + e = Cr(iii)$ $\quad E = +0.368$

(The maximum value as determined by me, of E_o for Cr(ii).Cr(iii) system in acid solution at a platinum electrode is taken here (vide page No.)

Hence E_q in the system (a) $= \frac{-0.153 + 0.368}{2} = 0.1075$ V.

E_q " " (b) $= \frac{-0.521 + 0.368}{2} = -0.0765$ V.

The sharpness of the sucessive breaks and the devi a-tion from the theoretical equivalence potential in the titration between copper sulphate and chromous chloride in presence of acids and salts and at different temperatures are likely to point towards the ideal condition required for the utility of chromous chloride as an analytical reagent.

Experimental:

A fresh 'neutral' solution of chromous chloride was prepared and transferred to the storage vessel with micro-burette arrangement and its strength determined using standard permanganate and ferrous ammonium sulphate. An exactly M/10 solution of copper sulphate was prepared from A.R. sample and its strength determined iodometrically. 3.0 N solutions of all the other reagents were prepared from A.R. samples by dissolving the calculated amounts in air free distilled water.

5.0 c.c. of copper sulphate solution was taken in the air tight titration cell, varying amounts of the reagent added in succession and the total volume made upto 30 c.c. with requisite amount of air free water. The air in the cell was then completely

displaced by passing a current of nitrogen for about half an hour and the mixture was titrated against chromous chloride solution using the automatic microburette attached to the storage assembly a smooth platinum wire electrode in conjunction with a s.c.e. was used to record the potentials. The current of nitrogen was used for stirring the mixture after each addition of chromous chloride and the inlet tube of the gas raised and kept above the solution while taking the readings in order to avoid stirring but at the same time to keep the nitrogen current through out the experiment

The strength of chromous chloride solution was checked up frequently by the potassium permanganate method. (Further confirmation was made by comparing the readings from the two breaks for the reduction of Cu(ii)). The readings are enetered as below:

Volume of $KMnO_4$ solution taken = 10.0 c.c.

Volume of $CrCl_2$ solution added = 2.0 c.c.

Strength of permanganate = 0.095 N

Volume of ferrous solution required for the reduction of unused $KMnO_4$ = 4.55 c.c.

Volume of ferrous solution equivalent to 10 c.c. of permanganate solution = 10.75 c.c.

Volume of ferrous solution equivalent to 2.0 c.c. of chromous chloride = 10.75 -4.55 = 6.2 cc

Strength of chromous chloride solution = 0.2739 N

Estimation of total chromium:

Volume of chromous chloride used for oxidation = 1.0 c.c.

Volume of ferrous solution required (determined potentiometrically) = 10.70 c.c.

Concentration of chromium in moles/litre = 0.3152

Ratio Cr(iii)/Cr(ii):

Concentration of Cr(iii) in the sample = 0.0413

The ratio of Cr(iii)/Cr(ii) = 0.1508

Titrations of $CuSO_4$ against chromous chloride under varying conditions:

Strength of copper sulphate = 0.1 M

Volume of copper sulphate taken for each titration = 5.0 c.c.

Total volume made up (with reagent and H_2O) = 30.0 c.c.

Strength of the reagent (original) in each case (except Na_2SO_4 where it is 2 M) = 3.0 N

Titration in neutral medium:

5 c.c. $CuSO_4$ + 25 c.c. water in the titration cell.

Temperature = 24°C

TABLE XXVIII.

Volume of $CrCl_2$	Observed potential	$\Delta E/\Delta c$
0.00 cc.	-0.3150	
0.50 "	-0.0600	
1.00 "	-0.0620	
1.50 "	-0.0615	1
1.70 "	-0.0419	10.2
1.80 "	-0.0150	26.0
1.85 "	-0.0115	7.0
1.90 "	-0.0050	
2.00 "	-0.0050	
3.00 "	-0.0155	
3.50 "	-0.0050	21.0
3.60 "	0.0500	55.0
3.65 "	0.1750	250.0
3.70 "	0.2055	61.0
3.80 "	0.2210	
4.00 "	0.2305	

Break	1	2
Volume of $CrCl_2$	1.75 cc.	3.65 cc.
Strength of $CrCl_2$	0.2858 N	0.2739 N

(vide curve No. 16)

Titrations in presence of varying amount of HCl.

TABLE XXIX

5 cc. $CuSO_4$ + 1 cc. HCl + 24 cc H_2O
Strength of HCl = 0.1 N

Vol. of CrCl	Potential	ΔE/c
-	-0.375	
0.5 cc.	-0.130	
1.0 cc.	-0.105	
1.5 cc.	-0.085	
1.7 cc.	-0.065	10
1.8 cc.	-0.030	35
1.9 cc.	-0.021	9
2.0 cc.	-0.015	
3.0 cc.	-0.005	
3.5 cc.	0.021	52
3.6 cc.	0.040	19
3.7 cc.	0.305	265
3.8 cc.	0.325	20
4.0 cc.	0.335	

Break	1	2
Vol. of $CrCl_2$	= 1.78 cc.	3.65 cc.
Strength of $CrCl_2$	= 0.2809 N	0.2739 N

(Vide curve no. 17)

TABLE XXX

5 cc. $CuSO_4$ + 2 cc. HCl + 23 cc H_2O
Strength of HCl = 0.2 N

Vol. of CrCl	Potential	ΔE/c
-	-0.385	
0.5 cc.	-0.145	
1.0 cc.	-0.130	
1.5 cc.	-0.122	
1.7 cc.	-0.103	9.5
1.8 cc.	-0.061	42.0
1.9 cc.	-0.042	19.0
2.0 cc.	-0.038	
3.0 cc.	-0.031	
3.5 cc	0.002	6.5
3.6 cc.	0.021	19.0
3.7 cc.	0.305	284
3.8 cc.	0.325	20
4.0 cc.	0.332	

Break	1	2
Vol. of $CrCl_2$	= 1.80 cc	3.72 cc.
Strength of $CrCl_2$	= 0.2877 N	0.2688 N

(Vide curve no. 18)

TABLE NO. XXXI.

5.0 cc. $CuSO_4$ + 5 cc. HCl + 20 cc H_2O

Strength of HCl = 0.5 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
0		+0.215	
0.5	cc.	-0.180	
1.0	"	-0.152	
1.5	"	-0.135	
1.7	"	-0.127	4
1.8	"	-0.102	25
1.9	"	-0.053	46
2.0	"	-0.031	8
2.5	"	-0.019	
3.5	"	0.003	
3.6	"	0.014	11
3.7	"	0.032	18
3.8	"	0.281	249
4.0	"	0.334	27

Break	1	2
Vol. of $CrCl_2$	1.725	3.75
Strength of $CrCl_2$	0.1725	0.375 N

(Vide Curve No. 19)

TABLE NO. XXXII.

5.0 cc. $CuSO_4$ + 10 cc. HCl + 15 cc H_2O

Strength of HCl = 1.0 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
0		-0.380	
0.5	cc.	-0.152	
1.0	"	-0.175	
1.5	"	-0.155	
1.7	"	-0.147	
1.8	"	-0.124	23
1.9	"	-0.087	37
2.0	"	-0.076	11
2.5	"	-0.023	
3.5	"	0.057	
3.6	"	0.066	9
3.7	"	0.072	32
3.8	"	0.344	272
4.0	"	0.273	17

Break	1	2
Vol. of $CrCl_2$	1.85	3.75
Strength of $CrCl_2$	0.185	0.375 N

(Vide Curve No.20)

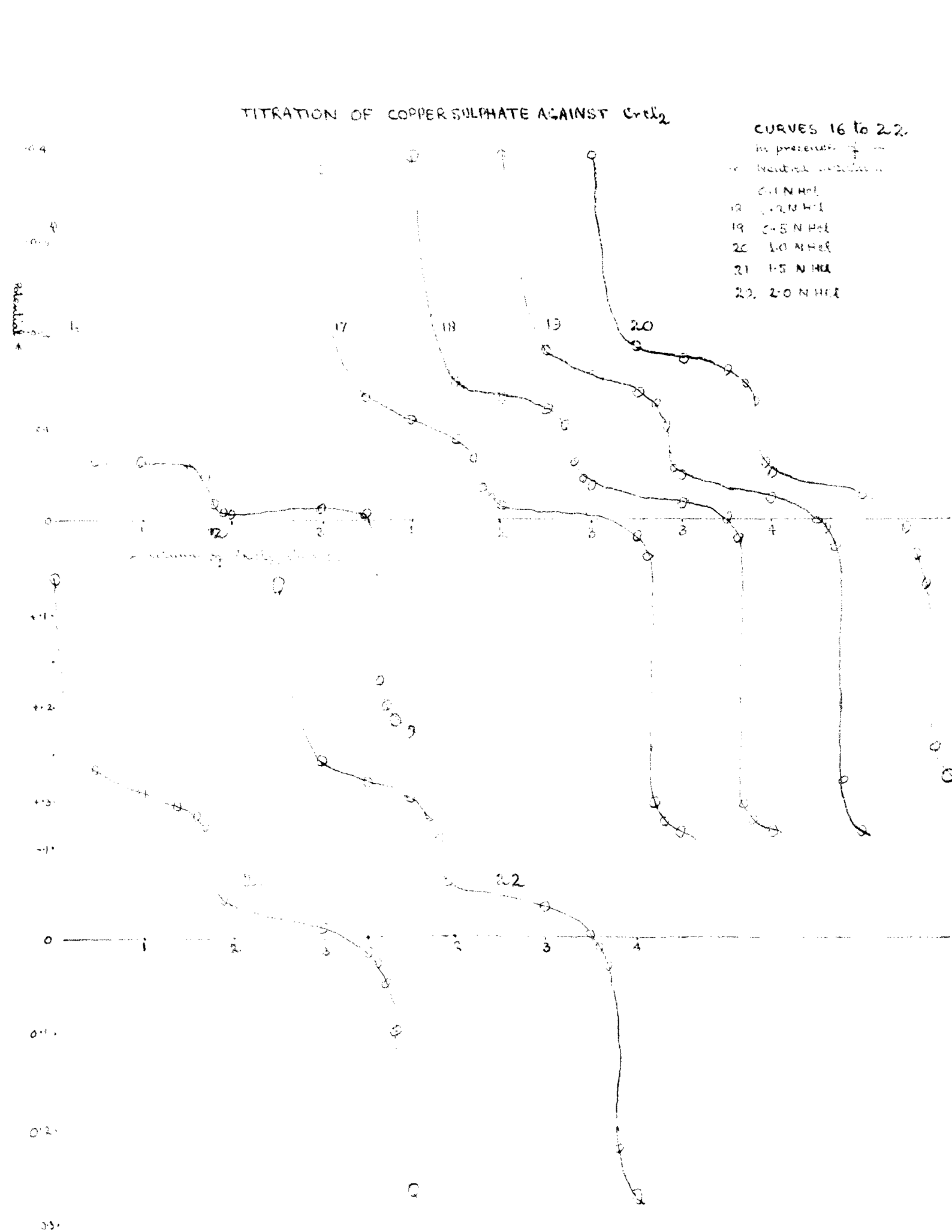

TITRATION OF COPPER SULPHATE AGAINST $CrCl_2$
CURVES 16 to 22.
In presence of —
Neutral solution +
0·1 N HCl
0·2 N HCl
0·5 N HCl
1·0 N HCl
1·5 N HCl
2·0 N HCl
16
17
18
19
20
21
22
potential

TABLE XXXIII

5 c.c. $CuSO_4$ + 15 c.c. HCl + 10 c.c. H_2O

Strength of HCl = 1.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.391	
0.5 c.c.	-0.102	
1.0 "	-0.154	
1.4 "	-0.146	
1.6 "	-0.138	
1.7 "	-0.123	15
1.8 "	-0.100	23
1.9 "	-0.041	59
2.0 "	-0.033	8
3.0 "	-0.011	
3.5 "	0.013	
3.6 "	0.032	19
3.7 "	0.050	18
3.8 "	0.102	52
4.0 "	0.267	82.5

Break	1	2
Strength of $CrCl_2$	= 0.2732 N	0.2632 N
Vol. of $CrCl_2$ =	1.83	3.8

(Vide curve No. 21)

TABLE XXXIV

5 c.c. $CuSO_4$ + 20 c.c. HCl + 5 c.c. H_2O

Strength of HCl = 2.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.386	
0.5 c.c.	-0.190	
1.0 "	-0.168	
1.5 "	-0.151	
1.7 "	-0.130	
1.8 "	-0.105	25
1.9 "	-0.058	47
2.0 "	-0.050	8
3.0 "	-0.032	
3.5 "	-0.003	
3.6 "	0.011	8
3.7 "	0.034	23
3.8 "	0.225	1 91
4.0 "	0.274	24.5

Break	1	2
Strength of $CrCl_2$	= 0.2748 N	0.2631
Vol. of $CrCl_2$ =	1.82	3.8

(Vide curve No. 22)

Titrations in precence of varying amounts of KCl:

TABLE XXXV.

5 c.c. $CuSO_4$ + 1 c.c. KCl + 24 c.c. H_2O

Strength of KCl = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E / \Delta c$
-	-0.282	
0.5 c.c.	-0.123	
1.0 "	-0.103	
1.55 "	-0.075	
1.7 "	-0.068	18
1.8 "	-0.021	27
1.9 "	-0.015	6
2.0 "	-0.015	
3.0 "	-0.018	
3.5 "	+0.020	7.5
3.6 "	0.068	48
3.75 "	0.312	162
4.0 "	0.340	72

666666

Break	1	2
Vol. of $CrCl_2$ =	1.75	3.6
Strength of $CrCl_2$ =	0.2809 N	0.2777 N

(Vide curve No. 23)

TABLE XXXVI.

5 c.c. $CuSO_4$ + 1 c.c. KCl + 23 c.c. H_2O

Strength of KCl = 0.2 N

Vol. of $CrCl_2$	Potential	$\Delta E / \Delta c$
-	-0.321	
0.6	-0.142	
1.0	-0.125	
1.5	-0.108	
1.7	-0.090	9
1.8	-0.048	42
1.9	-0.041	7
2.0	-0.034	
3.0	-0.035	
3.5	0.005	
3.6	0.056	51
3.65	0.136	240
3.7	0.230	108
3.8	0.276	46
4.0	0.305	

Break	1	2
Vol. of $CrCl_2$ =	1.78	3.65
Strength of $CrCl_2$ =	0.2809 N	0.2739 N

(Vide curve No. 24)

TABLE XXXVII

5 c.c. $CuSO_4$ + 5 c.c. KCl + 20 c.c. H_2O

Strength of KCl = 0,5 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.330	
0.5	c.c.	-0.161	
1.1	"	-0.139	
1.5	"	-0.126	
1.7	"	-0.113	6.5
1.8	"	-0.089	24
1.9	"	-0.051	38
2.0	"	-0.050	1
3.0	"	-0.048	
3.6	"	-0.031	
3.6	"	-0.012	19
3.7	"	0.049	61
3.8	"	0.204	155
4.0	"	0.291	43

Break	1	2
Vol. of $CrCl_2$ =	1.8	3.73
Strength =	0.2777 N	0.2681 N

(Vide curve No. 25)

TABLE XXXVIII

5 c.c. $CuSO_4$ + 10 c.c. KCl + 15 c.c. H_2O

Strength of KCl = 1.0 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.340	
0.5	c.c.	-0.171	
1.0	"	-0.150	
1.5	"	-0.138	
1.75	"	-0.113	10
1.85	"	-0.064	49
2.0	"	-0.053	4.4
3.0	"	-0.051	
3.5	"	-0.026	
3.6	"	-0.001	25
3.7	"	0.049	50
3.8	"	0.201	152
4.0	"	0.266	32.5

Break	1	2
Vol. of $CrCl_2$ =	1.8	3.75
Strength =	0.2777 N	0.2667 N

(Vide curve No. 26)

TABLE NO. XXXIX.

5 c.c. $CuSO_4$ + 15 c.c. KCl
+ 10 c.c. H_2O

Strength of KCl = 1.5 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.331	
0.6	c.c.	-0.176	
1.0	"	-0.162	
1.5	"	-0.151	
1.7	"	-0.142	
1.8	"	-0.123	19
1.9	"	-0.081	42
2.1	"	-0.068	6.5
3.0	"	-0.056	
3.5	"	-0.018	
3.6	"	0.006	24
3.7	"	0.046	40
3.8	"	0.201	155
4.0	"	0.252	25.5

Break	1	2
Vol. of $CrCl_2$ =	1.83	3.8
Strength =	0.2732 N	0.2631 N

(Vide cureve No. 27)

TABLE NO. XL.

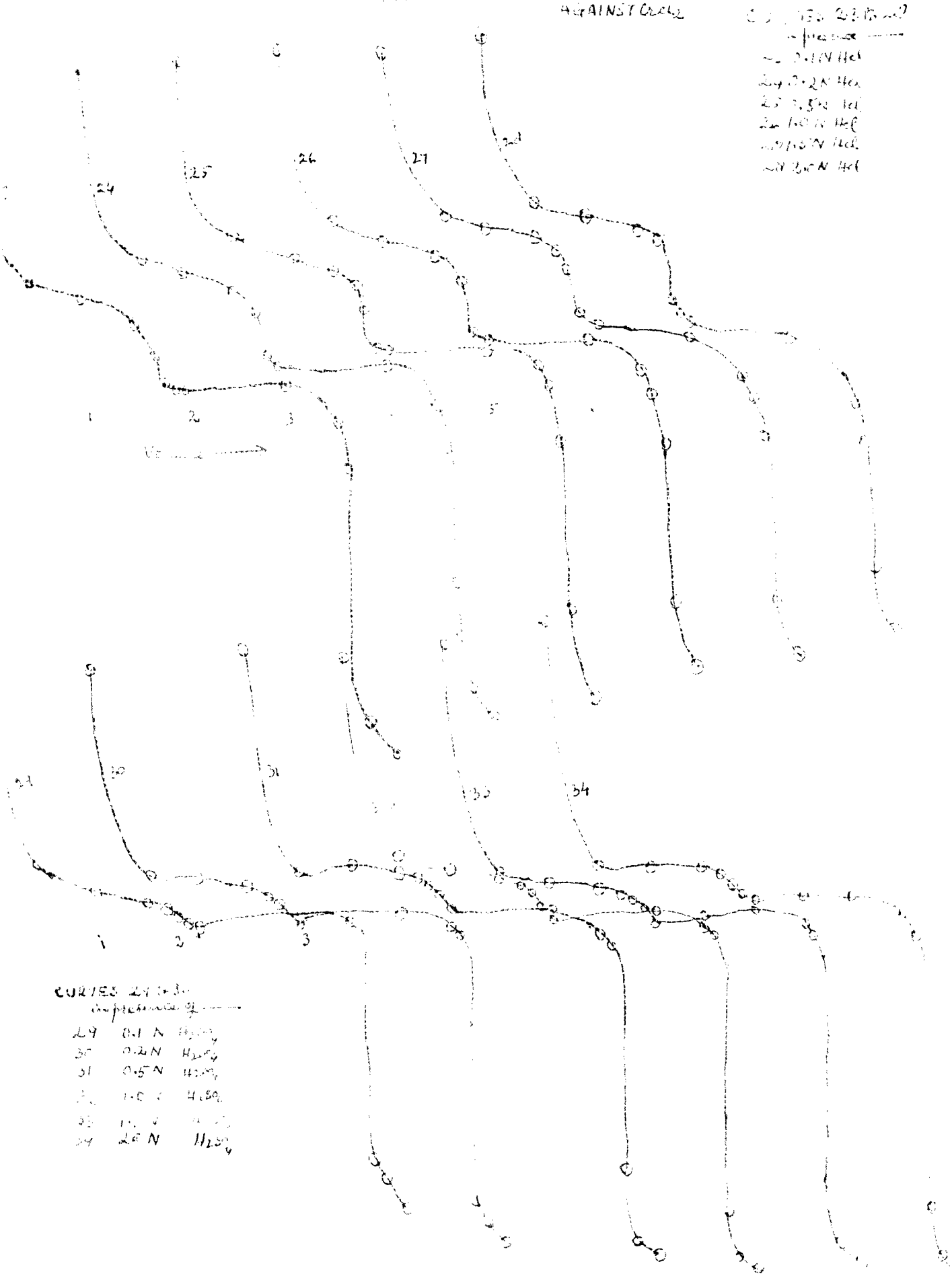
5 c.c. $CuSO_4$ + 20 c.c. KCl
1 + 5 c.c. H_2O

Strength of KCl = 2.0 N.

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.348	
0.5	c.c.	-0.185	
1.0	"	-0.171	
1.5	"	-0.156	
1.7	"	-0.148	4
1.8	"	-0.088	60
1.9	"	-0.076	12
2.0	"	-0.071	
3.0	"	-0.050	
3.5	"	-0.011	
3.6	"	0.016	27
3.7	"	0.052	36
3.8	"	0.166	114
4.0	"	0.234	39

Break	1	2
Vol. of $CrCl_2$ =	1.80	3.8
Strength =	0.2777 N	0.2631 N

(Vide curve No. 28)


TITRATION OF COPPER SULPHATE
AGAINST
24
25
26
27
1
2
3
30
31
34
1
2
3

Readings with H_2SO_4.

TABLE XLI.

5 c.c. $CuSO_4$ + 1 c.c. H_2SO_4 + 24 c.c. H_2O

Strength of H_2SO_4: 0.1 N

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.226	
0.4	cc.	-0.035	
1.0	"	-0.035	
1.5	"	-0.025	
1.7	"	-0.019	3
1.8	"	-0.011	8
1.9	"	-0.004	7
2.0	"	-0.001	3
3.0	"	-0.005	
3.5	"	-0.002	
3.6	"	0.005	7
3.7	"	0.219	217
3.8	"	0.235	16
4.0	"	0.232	

Mean 1 2

Vol. of $CrCl_2$ = 1.85 3.65

Strength = 0.2703 N 0.2739 N

(Vide curve No.29)

TABLE XLII.

5 c.c. $CuSO_4$ + 2 c.c. H_2SO_4 + 23 c.c. H_2O

Strength of H_2SO_4: 0.2 N.

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.252	
0.52	cc.	-0.051	
1.0	"	-0.050	
1.5	"	-0.038	
1.7	"	-0.026	5.8
1.8	"	-0.020	6.2
1.9	"	-0.006	14
2.0	"	-0.001	5
2.02	"	-0.002	
2.5	"	0.004	
2.6	"	0.009	5
2.7	"	0.260	251
2.8	"	0.279	19
4.0	"	0.301	

Mean 1 2

Vol. of $CrCl_2$ = 1.83 3.65

Strength = 0.2732 N 0.2739 N

(Vide curve No.30)

TABLE XLIII.

5 c.c. $CuSO_4$ + 5 c.c. H_2SO_4 + 20 c.c. H_2O

Strength of H_2SO_4 = C.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.266	
0.5 c.c.	-0.051	
1.05 "	-0.055	
1.5 "	-0.049	
1.7 "	-0.045	2
1.81 "	-0.036	4.4
1.9 "	-0.009	10.4
2.0 "	-0.009	18
3.02 "	-0.010	
3.5 "	0.016	
3.6 "	0.024	8
3.71 "	0.231	2
3.8 "	0.310	4.5

Break	1	2
Vol. of $CrCl_2$	= (1.085)	3.7
Strength of $CrCl_2$	= 0.2703 N	0.2703 N

(Vide curve No. 31)

TABLE XLIV.

5 c.c. $CuSO_4$ + 10 c.c. H_2SO_4 + 15 c.c. H_2O

Strength of H_2SO_4 = 1.0 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.252	
0.5 c.c.	-0.062	
1.0 "	-0.050	
1.5 "	-0.041	
1.7 "	-0.034	3.5
1.8 "	-0.025	9
1.91 "	-0.016	8.2
2.0 "	-0.001	1.9
3.0 "	-0.005	
3.5 "	0.006	
3.6 "	0.011	5
3.71 "	0.275	240
4.0 "	0.329	

Break	1	2
Vol. of $CrCl_2$	= (1.90)	3.72
Strength of $CrCl_2$	= 0.2631 N	0.2688 N.

(Vide curve No. 32)

TABLE XLV.

5 c.c. $CuSO_4$ + 15 c.c. H_2SO_4 + 10 c.c. H_2O

Strength of H_2SO_4 = 1.5 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
0	-0.270	
0.41 c.c.	-0.060	
1.0 "	-0.057	
1.5 "	-0.028	
1.7 "	-0.022	
1.9 "	-0.017	5
1.9 "	-0.005	12
2.0 "	0.004	9
2.5 "	0.000	
2.9 "	-0.003	
3.5 "	0.000	
3.9 "	0.004	12
3.7 "	0.250	246
3.8 "	0.303	64
4.0 "	0.325	

Vol. of $CrCl_2$ = 1.25 3.7

Strength = 0.2703 N 0.2703 N

(Vide curve No. 33)

TABLE XLVI.

5 c.c. $CuSO_4$ + 20 c.c. H_2SO_4 + 5 c.c. H_2O

Strength of H_2SO_4 = 2.0 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
0	-0.721	
0.5 c.c.	-0.051	
1.02 "	-0.049	
1.5 "	-0.048	
1.7 "	-0.030	
1.8 "	-0.031	8
1.9 "	-0.020	10
2.0 "	-0.015	4.4
2.3 "	-0.021	
3.0 "	-0.015	
3.5 "	0.000	
3.6 "	0.020	10.2
3.7 "	0.276	204
3.8 "	0.320	44
4.0 "	0.[illegible]	

Vol. of $CrCl_2$ = 1.00 3.70

Strength = 0.2331 N 0.2331 N

(Vide curve No. 34)

Titrations in presence of varying amounts of Na_2SO_4:

TABLE XLVII.

5. c.c. $CuSO_4$ + 1 c.c. Na_2SO_4 + 14 c.c. H_2O

Strength of Na_2SO_4 = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.198	
0.5 c.c.	-0.048	
0.98 "	-0.031	
1.5 "	-0.025	
1.7 "	-0.021	2
1.8 "	-0.012	8.2
1.9 "	-0.002	10
2.0 "	0.003	5
3.0 "	0.011	
3.5 "	0.024	
3.6 "	0.031	8
3.7 "	0.252	221
3.8 "	0.290	38
4.0 "	0.305	

Break	1	2
Vol. of $CrCl_2$ =	1.9	3.68
Strength =	0.2631 N	0.2717 N

(Vide curve No.35)

TABLE XLVIII.

5 c.c. $CuSO_4$ + 2 c.c. Na_2SO_4 + 13 c.c. H_2O

Strength of Na_2SO_4 = 0.2 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.211	
0.5 c.c.	-0.045	
1.0 "	-0.048	
1.5 "	-0.041	
1.7 "	-0.032	4.5
1.8 "	-0.020	12
1.9 "	-0.003	17
2.0 "	0.000	3
2.5 "	0.011	
3.0 "	0.100	
3.5 "	0.025	
3.6 "	0.034	9
3.7 "	0.231	197
3.8 "	0.312	81
4.0 "	0.330	

Break	1	2
Vol. of $CrCl_2$ =	1.95	3.7
Strength =	0.2564 N	0.2703

(Vide curve No. 36)

TABLE XLIX

5 c.c. $CuSO_4$ + 5 c.c. Na_2SO_4 → 10 c.c. H_2O

Strength of Na_2SO_4 = 0.5 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.228	
0.5 c.c.	-0.042	
1.01 "	-0.031	
1.3 "	-0.022	
1.7 "	-0.019	1.5
1.8 "	-0.015	4
1.9 "	-0.011	4
2.02 "	-0.002	7.5
3.0 "	0.022	
3.5 "	0.034	
3.6 "	0.048	6
3.7 "	0.262	218
3.8 "	0.286	20
4.0 "	0.303	

Break 1

Vol. of $CrCl_2$ = - 3.7

Strength = " 0.2703 N

(Vide curve No. 38)

TABLE L

5 c.c. $CuSO_4$ → 10 c.c. Na_2SO_4 + 5 c.c. H_2O

Strength of Na_2SO_4 = 1.0 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.250	
0.5 cc.c	-0.053	
1.0 "	-0.033	
1.5 "	-0.024	
1.7 "	-0.018	3
1.8 "	-0.012	6
1.9 "	-0.005	7
2.0 "	0.000	5
2.5 "	0.021	
3.0 "	0.023	
3.5 "	0.049	
3.6 "	0.064	8
3.7 "	0.251	187
3.8 "	0.282	31
4.0 "	0.305	

Break 1 2

Vol. of $CrCl_2$ = - 3.68

Strength = " 0.2717 N

(Vide curve No. 38)

TABLE LI.

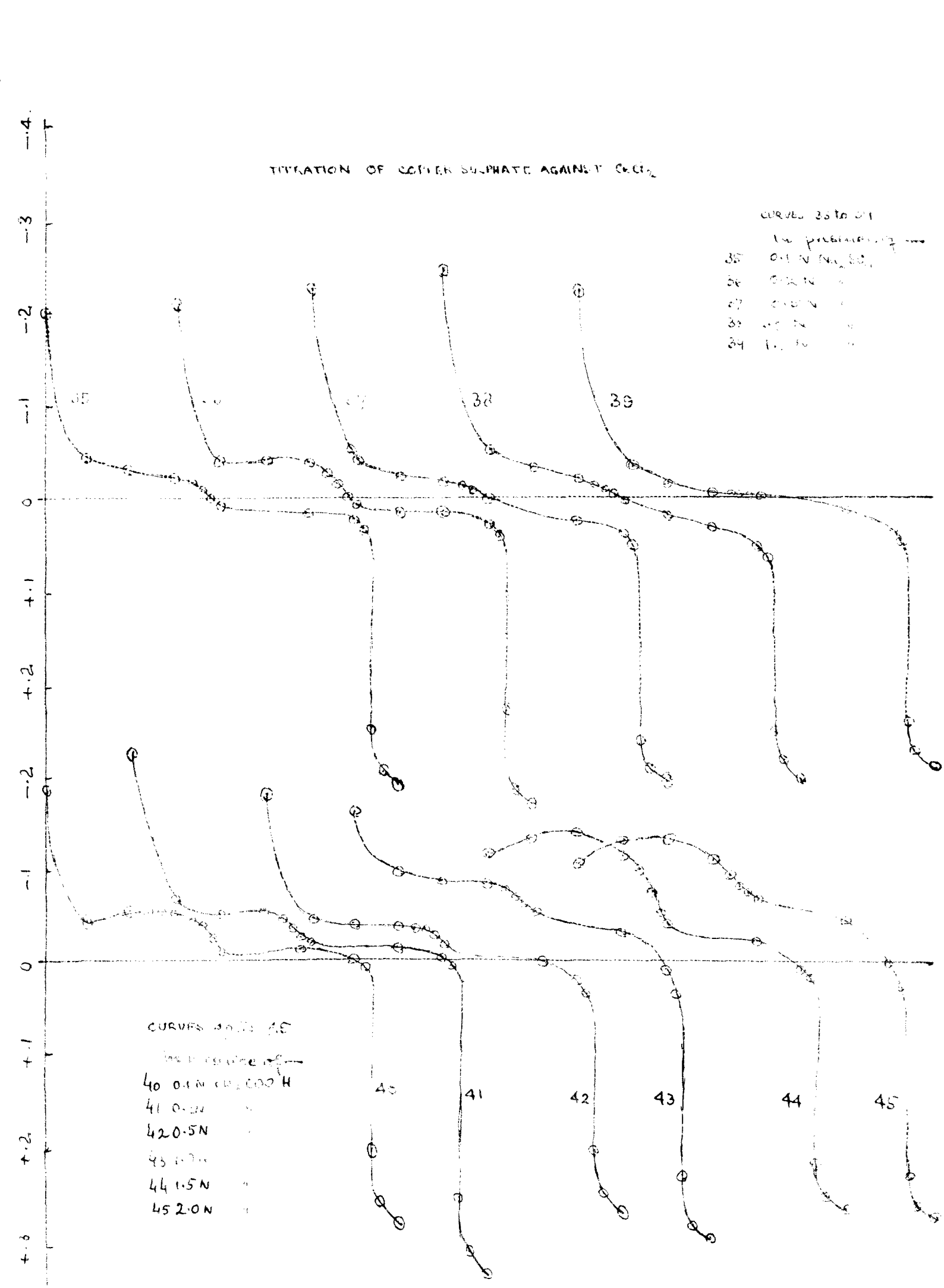
5 c.c. $CuSO_4$ + 15 c.c. Na_2SO_4 + 0 cc. H_2O

Strength of Na_2SO_4 = 0.5 N.

Vol. of $CrCl_2$		Potential	$\Delta E/\Delta c$
-		-0.226	
0.6	c.c.	-0.042	
1.0	"	-0.021	
1.5	"	-0.009	
1.7	"	-0.003	3
1.8	"	-0.002	1
1.9	"	-0.002	0
2.0	"	-0.001	
3.0	"	0.015	
3.5	"	0.033	
3.6	"	0.046	13
3.7	"	0.236	173
3.8	"	0.270	38
4.0	"	0.286	

Break		1	2
Vol. of $CrCl_2$	=	-	3.70
Strength	=	-	0.2703 N

(Vide curve No. 39)


TITRATION OF COPPER SULPHATE AGAINST
CURVES 35 to 39
35
36
37
38
39
CURVES 40 TO 45
40 0.1 N
41
42 0.5 N
43
44 1.5 N
45 2.0 N

Titrations in presence of varying amount of acetic acid.

TABLE LII.

5 c.c. $CuSO_4$ + 1 c.c. HAc + 24 c.c. H_2O

Strength of HAc = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.192	
0.5 c.c.	-0.049	
1.0 "	-0.051	
1.49 "	-0.050	
1.7 "	-0.045	
1.8 "	-0.041	4
1.9 "	-0.025	16
2.0 "	-0.011	14
3.01 "	-0.012	
3.5 "	0.000	
3.6 "	0.008	3
3.7 "	0.205	202
3.8 "	0.261	56
4.0 "	0.274	

Break	1	2
Vol. of $CrCl_2$ =	(1.9)	3.7
Strength =	(0.2631 N)	(0.2703 N

(Vide curve No. 40)

TABLE LIII.

5 c.c. $CuSO_4$ + 2 c.c. HAc + 23 c.c. H_2O

Strength of HAc = 0.2 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.224	
0.5 c.c.	-0.071	
1.0 "	-0.052	
1.5 "	-0.054	
1.7 "	-0.048	3
1.8 "	-0.037	11
1.9 "	-0.025	12
2.0 "	-0.020	4.5
3.0 "	-0.016	
3.5 "	-0.004	
3.6 "	0.000	4
3.7 "	0.249	149
3.8 "	0.306	57
4.0 "	0.331	

Break	1	2
Vol. of $CrCl_2$ =	(1.93)	3.72
Strength =	(0.2576 N)	0.2688 N

(Vide cureve No. 41)

TABLE LIV.

5 c.c. $CuSO_4$ + 5 c.c. HAc
+ 20 c.c. H_2O

Strength of HAc = 0.5 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.181	
0.54 c.c.	-0.048	
1.0 "	-0.041	
1.5 "	-0.035	
1.7 "	-0.032	
1.8 "	-0.031	1
1.9 "	-0.076	5
2.0 "	-0.018	8
3.1 "	-0.001	
3.6 "	0.021	
3.8 "	0.035	15
3.7 "	0.203	167
3.8 "	0.223	41
4.0 "	0.265	

Break	1	2
Vol. of $CrCl_2$=	(1.95)	3.38
Strength	= 0.2564 N	0.1737 N

(Vide curve No. 42)

TABLE LV.

5 c.c. $CuSO_4$ + 10 c.c. HAc
+ 23 c.c. H_2O

Strength of HAc = 1.0 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.162	
0.5 c.c.	-0.096	
1.0 "	-0.090	
1.51 "	-0.083	
1.7 "	-0.076	
1.8 "	-0.071	5
1.9 "	-0.063	8
2.0 "	-0.054	9
3.0 "	-0.032	
3.5 "	0.005	
3.6 "	0.054	29
3.7 "	0.225	191
3.8 "	0.287	62
4.0 "	0.300	

Break	1	2
Vol. of $CrCl_2$=	-	3.7
Strength	=	0.700 N

(Vide curve No. 43)

TABLE LVI.

£5 c.c. $CuSO_4$ + 15 c.c. HAc
+ 10 c.c. H_2O

Strength of HAc = 1.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	+0.120	
0.52 c.c.	-0.034	
1.01 "	-0.141	
1.5 "	-0.112	
1.7 "	-0.096	8
1.8 "	-0.081	15
1.9 "	-0.075	6
2.0 "	-0.071	
3.0 "	-0.044	
3.5 "	-0.000	14
3.6 "	-0.014	201
3.7 "	0.215	35
3.8 "	0.250	
4.0 "	0.263	

Break	1	2
Vol. of $CrCl_2$	= (1.9)	3.72
Strength	= 0.2631 N	0.2688

(Vide curve No. 44)

TABLE LVII.

5 c.c. $CuSO_4$ + 20 c.c. HAc
+ 5 c.c. H_2O

Strength of HAc = 2.0 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.108	
0.5 c.c.	-0.130	
1.0 "	-0.132	
1.5 "	-0.110	
1.7 "	-0.086	8
1.8 "	-0.078	18
1.9 "	-0.074	4
2.0 "	-0.070	
3.0 "	-0.045	
3.5 "	0.002	
3.6 "	0.025	23
3.7 "	0.226	221
3.8 "	0.261	35
4.0 "	0.274	

Break	1	2
Vol. of $CrCl_2$	-	3.68
Strength	-	0.2717 N

(Vide curve No. 45)

Titrations in presence of varying amounts of sodium acetate:

TABLE LVIII

5 c.c. $CuSO_4$ + 1 c.c. NaHc + 24 c.c. H O

Strength of NaHc = 0.1 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.181	
0.5 c.c.	-0.034	
1.0 "	-0.020	
1.5 "	-0.020	
1.7 "	-0.020	0
1.8 "	-0.018	2.2
1.9 "	-0.015	3
2.0 "	-0.012	3
3.0 "	-0.010	
3.5 "	-0.005	
3.6 "	-0.003	1.9
3.7 "	0.002	5.5
3.8 "	0.054	58
4.0 "	0.131	39

Break 1 2

Vol. od $CrCl_2$ = - 3.85

Strength = - 0.2597 N

(Vide curve No.46)

TABLE LIX

5 c.c. $CuSO_4$ + 2 c.c. NaHc + 23 c.c. H O

Strength of NaHc = 0.2 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.110	
0.51 c.c.	-0.024	
1.0 "	-0.021	
1.5 "	-0.020	
1.7 "	-0.018	
1.8 "	-0.017	
1.9 "	-0.015	
2.0 "	-0.012	
3.0 "	-0.015	
3.5 "	-0.014	
3.6 "	-0.012	
3.7 "	-0.010	
3.8 "	-0.003	
4.0 "	0.008	
4.5 "	0.075	

No good break in either stage

(Vide curve No.47)

Titrations in presence of KCl & HCl.

TABLE LX

5 c.c. $CuSO_4$ + 1 c.c. HCl
+ 1 c.c. KCl + 23 c.c. H_2O

Strength of HCl = 0.1 N
" " KCl = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.231	
0.5 c.c.	-0.067	
1.02 "	-0.060	
1.5 "	-0.061	
1.7 "	-0.047	7
1.8 "	-0.031	16
1.9 "	-0.025	6
2.0 "	-0.021	
2.5 "	-0.022	
3.0 "	-0.025	
3.6 "	-0.008	17
3.6 "	0.001	220
3.7 "	0.221	38
3.8 "	0.259	
4.0 "	0.275	

Break	1	2
Vol. of $CrCl_2$ =	1.75	3.65
Strength =	0.2858 N	0.2739 N

(Vide curve No.. 48)

TABLE LXI

5 c.c. $CuSO_4$ + 1 c.c. HCl
+ 10 c.c. KCl + 14 c.c. H_2O

Strength of HCl = 0.1 N
" " KCl = 1.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.287	
0.51 c.c.	-0.091	
1.0 "	-0.075	
1.52 "	-0.062	
1.7 "	-0.058	8
1.8 "	-0.031	27
1.9 "	-0.010	21
2.0 "	-0.012	
2.5 "	-0.014	
3.0 "	-0.021	
3.5 "	-0.013	
3.6 "	0.002	15
3.7 "	0.025	23
3.8 "	0.231	206
4.0 "	0.264	16.5

Break	1	2
Vol. of $CrCl_2$ =	1.82	3.75
Strength =	0.2748 N	0.2667 N

(Vide curve No. 49)

TABLE LXII

5 c.c. $CuSO_4$ + 10 c.c. HCl
+ 1 c.c. KCl + 14 c.c. H_2O
Strength of HCl = 1.0 N
" " KCl = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.308	
0.5 c.c.	-0.101	
1.02 "	-0.096	
1.5 "	-0.091	
1.7 "	-0.082	
1.8 "	-0.061	21
1.9 "	-0.023	38
2.0 "	-0.020	3
2.5 "	-0.021	
3.0 "	-0.025	
3.5 "	-0.013	
3.6 "	-0.001	
3.7 "	-0.015	18
3.8 "	0.211	196
4.0 "	0.249	19

Break	1	2
Vol. of $CrCl_2$ =	1.83	3.75
Strength =	0.2732 N	0.2667 N

(Vide curve No. 50)

TABLE LXIII

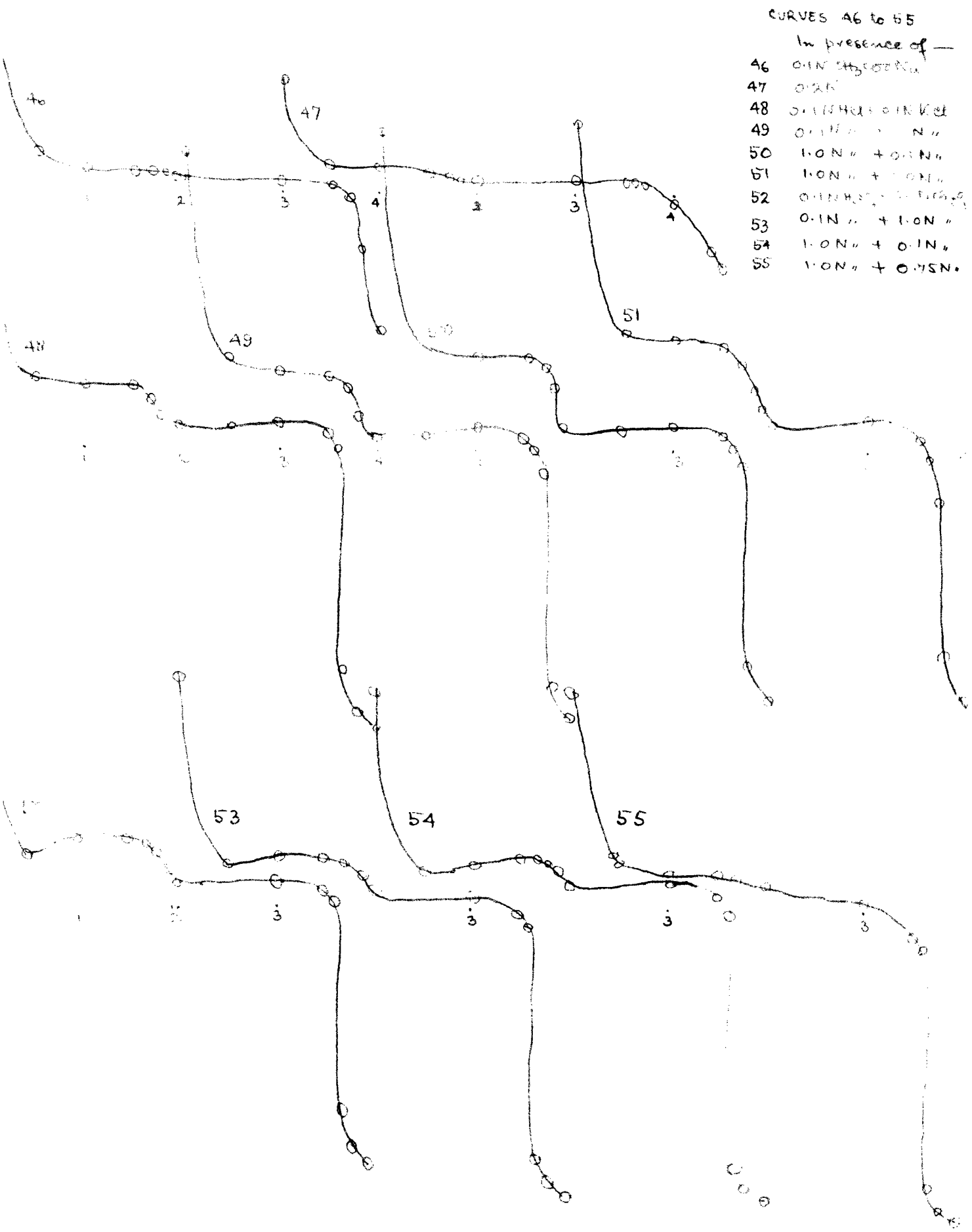
5 c.c. $CuSO_4$ + 10c.c. HCl
+ 10 KCl + 5 c.c. H_2O
Strength of HCl = 1.0 N
" " KCl = 1.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.318	
0.51 c.c.	-0.117	
1.0 "	-0.111	
1.5 "	-0.102	
1.7 "	-0.086	
1.8 "	-0.059	27
1.9 "	-0.036	23
2.0 "	-0.025	11
3.0 "	-0.029	
3.5 "	-0.011	
3.6 "	0.010	
3.7 "	0.051	45
3.8 "	0.202	137
4.0 "	0.245	43

Break	1	2
Vol. of $CrCl_2$ =	1.82	3.8
Strength =	0.2748 N	0.2631 N

(Vide curve No. 51)

TITRATION OF COPPER SULPHATE AGAINST $CaCl_2$



Titrations in presence of H_2SO_4 & Na_2SO_4.

TABLE LXIV.

5 c.c. $CuSO_4$ + 1 c.c. H_2SO_4 + 2 c.c. Na_2SO_4 + 22 c.c. H_2O

Strength of H_2SO_4 = 0.1 N

" " Na_2SO_4 = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.251	
0.49 c.c.	-0.049	
1.0 "	-0.066	
1.5 "	-0.068	
1.7 "	-0.061	
1.8 "	-0.054	8
1.9 "	-0.035	19
2.0 "	-0.024	12
3.0 "	-0.025	
3.5 "	-0.014	
3.6 "	-0.006	8
3.7 "	0.197	203
3.8 "	0.228	31
4.0 "	0.239	
633		

Break	1	2
Vol. of $CrCl_2$ =	1.9	3.7
Strength =	0.2631 N	0.2703 N

(Vide curve No. 52)

TABLE LXV.

5 c.c. $CuSO_4$ + 1 c.c. H_2SO_4 + 20 c.c. Na_2SO_4 + 4 c.c. H_2O

Strength of H_2SO_4 = 0.1 N

" " Na_2SO_4 = 1.0 N.

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.225	
0.51 c.c.	-0.042	
1.02 "	-0.049	
1.5 "	-0.047	
1.7 "	-0.042	
1.8 "	-0.039	3
1.9 "	-0.030	9
2.0 "	-0.004	26
3.0 "	-0.009	
3.5 "	0.002	
3.6 "	0.021	17
3.7 "	0.191	189
3.8 "	0.230	32.5
4.0 "	0.242	
"		

Break	1	2
Vol. of $CrCl_2$ =	1.95	3.65
Strength =	0.2564 N	0.2739 N

(Vide curve No. 53)

Titrations in presence of acetic acid and sodium acetate:

TABLE LXVIII.

5 c.c. $CuSO_4$ + 1 c.c. HAc
+ 1 c.c. NaAc + 23 c.c. H_2O

Strength of HAc = 0.1 N
" " NaAc = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.178	
0.5 c.c.	-0.037	
1.0 "	-0.061	
1.49 "	-0.032	
1.7 "	-0.031	
1.8 "	-0.025	
1.9 "	-0.021	
2.0 "	-0.016	
3.02 "	-0.011	
3.5 "	-0.004	
3.6 "	0.002	
3.7 "	0.127	
3.8 "	0.152	
4.0 "	0.170	

6

Break	1	2
Vol. of $CrCl_2$ =	1.95	3.7
Strength =	0.2564 N	0.2703 N

(Vide curve No. 56)

TABLE LXIX

5 c.c. $CuSO_4$ + 10c.c. HAc
1 c.c. NaAc + 14 c.c. H_2O

Strength of HAc = 1.0 N
" " NaAc = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$	
-	-0.174		
0.51 c.c.	-0.038		
1.0 "	-0.041		
1.5 "	-0.045		
1.7 "	-0.042		1.5
1.8 "	-0.040		1
1.9 "	-0.036		4
2.0 "	-0.031		5
3.0 "	-0.017		
3.5 "	-0.012		
3.6 "	-0.002		10
3.7 "	0.014		16
3.8 "	0.118		94.5
4.0 "	0.0139		23

Break	1	2
Vol. of $CrCl_2$ =	-	(3.75)
Strength =	-	0.2667 N

(Vide curve No. 57)

TABLE LXVI

5 c.c. $CuSO_4$ + 2 c.c. Na_2SO_4 + 10 c.c. H_2SO_4 + 13 c.c. H_2O

Strength of H_2SO_4 = 1.0 N

" " Na_2SO_4 = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.210	
0.52 c.c.	-0.036	
1.01 "	-0.040	
1.5 "	-0.049	
1.7 "	-0.048	
1.8 "	-0.043	5
1.9 "	-0.032	11
2.02 "	-0.020	10
3.0 "	-0.024	
3.5 "	-0.014	
3.6 "	0.005	19
3.7 "	0.246	241
3.8 "	0.267	21
4.0 "	0.0274	

Break	1	2
Vol. of $CrCl_2$	= (1.95)	3.65
Strength	= (0.2564 N)	0.2739

(Vide curve No. 54)

TABLE LXVII

5 c.c. $CuSO_4$ + 10 c.c. H_2SO_4 + 15 c.c. Na_2SO_4

Strength of H_2SO_4 = 1 N

" " Na_2SO_4 = 0.75 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	0.203	
0.49 c.c.	-0.049	
1.03 "	-0.034	
1.5 "	-0.031	
1.7 "	-0.029	
1.8 "	-0.028	
1.9 "	-0.025	3.3
2.0 "	-0.018	7
3.0 "	-0.008	
3.5 "	0.024	
3.6 "	0.038	12.7
3.7 "	0.265	252
3.79 "	0.279	14
4.0 "	0.302	

Break	1	2
Vol. of $CrCl_2$	-	3.68
Strength	= -	

(Vide curve No. 55)

Titrations in presence of KCl & HAc:

TABLE LXX

5 c.c. $CuSO_4$ + 1 c.c. KCl + 1 c.c. HAc + 23 c.c. H_2O

Strength of KCl $\leq$ 0.1 N

" " HAc = 0.1 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.264	
0.52 c.c.	-0.086	
1.0 "	-0.085	
1.5 "	-0.085	
1.75 "	-0.074	
1.85 "	-0.069	5
2.0 "	-0.034	26
2.5 "	-0.029	1
3.0 "	-0.025	
3.5 "	-0.012	
3.6 "	-0.000	13.3
3.7 "	0.261	261
3.8 "	0.286	5
4.1 "	0.302	

Break	1	2
Vol. of $CrCl_2$ =	1.9	3.7
Strength =	0.2631 N	0.2703 N

(Vide curve No. 58)

TABLE LXXI

5 c.c. $CuSO_4$ + 15 c.c. KCl + 5 c.c. HAc + 5 c.c. H_2O

Strength of KCl = 1.5 N

" " HAc = 0.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.284	
0.5 c.c.	-0.096	
1.0 "	-0.084	
1.5 "	-0.075	
1.7 "	-0.073	
1.8 "	-0.070	3
1.85 "	-0.062	16
1.9 "	-0.054	16
2.0 "	-0.028	26
3.0 "	-0.025	
3.5 "	-0.025	
3.6 "	-0.021	
3.7 "	-0.0111	10
3.8 "	0.255	265
4.0 "	0.274	95

Break	1	2
Vol. of $CrCl_2$ $\leq$	1.85	3.8
Strength =	0.2739 N	0.2631 N

(Vide curve No. 59)

TABLE LXXII

5 c.c. $CuSO_4$ + 5 c.c. KCl + 15 c.c. HAc + 5 cc. H_2O

Strength of KCl = 0.5 N

" " HAc = 1.5 N

Vol. of $CrCl_2$	Potential	ΔE/ Δc
"	-0.301	
0.51 c.c.	-0.102	
1.02 "	-0.090	
1.5 "	-0.092	
1.7 "	-0.084	
1.8 "	-0.080	4
1.9 "	-0.073	6.4
2.0 "	-0.034	43
2.9 "	-0.030	
3.5 "	-0.005	
3.6 "	-0.026	21
3.7 "	-0.065	39
3.86 "	0.246	120.6
4.0 "	0.259	8.6

Break	1	2
Vol. of $CrCl_2$ =	1.85	3.75
Strength =	0.2703 N	0.2667 N

(Vide curve No. 60)

TABLE LXXIII

5 c.c. $CuSO_4$ + 10 c.c. KCl + 10 c.c. HAc + 5 c.c. H_2O

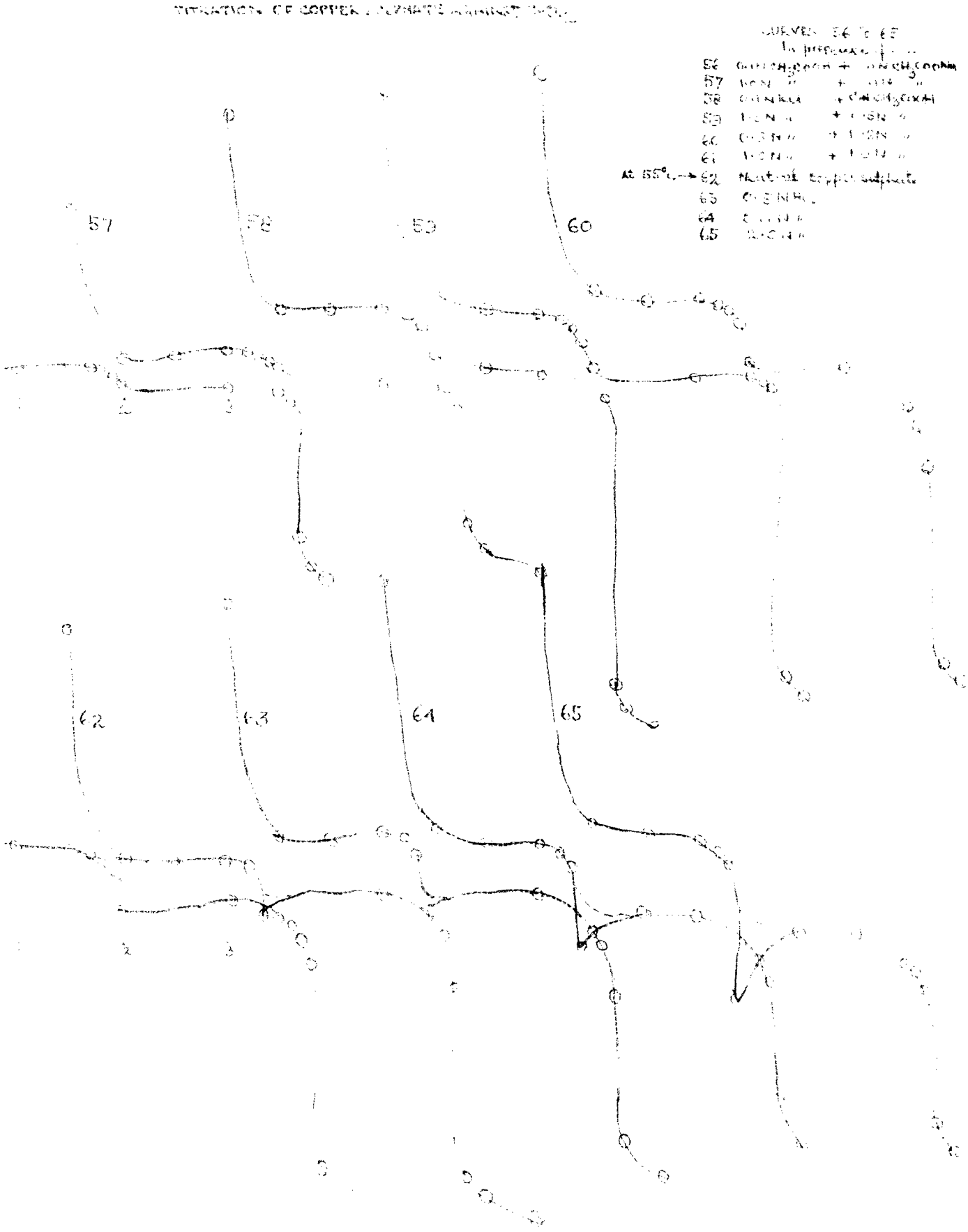
Strength of KCl = 1.0 N

" " HAc = 1.0 N

Vol. of $CrCl_2$	Potential	ΔE/ Δc
-	-0.321	
0.5 c.c.	-0.100	
1.0 "	-0.092	
1.5 "	-0.089	
1.69 "	-0.081	
1.8 "	-0.075	5.6
1.9 "	-0.058	17
2.0 "	-0.031	27
3.02 "	-0.039	
3.5 "	-0.025	
3.6 "	-0.016	
3.7 "	-0.003	13
3.8 "	0.021	24
3.9 "	0.204	183
4.0 "	0.225	7

Break	1	2
Vol of $CrCl_2$ =	1.85	3.9
Strength =	0.2703 N	0.2564 N

(Vide curve No. 61)


57
58
59
60
62
63
61
65

The following readings were taken at 55°C . The titration cell was kept in a water bath heated over a hot plate with regulator arrangement.

Titration in neutral medium:

TABLE LXXIV.

5 c.c. $CuSO_4$ + 25 c.c. H_2O

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.291	
0.55 c.c.	-0.076	
1.0 "	-0.075	
1.49 "	-0.074	
1.7 "	-0.071	1.4
1.85 "	-0.025	31
1.9 "	-0.035	20
2.0 "	-0.041	
2.1 "	-0.043	
3.0 "	-0.045	
3.5 "	-0.018	
3.6 "	-0.005	13
3.7 "	0.045	50
3.8 "	0.210	165
4.0 "	0.227	
4.5 "	0.251	

Break	1	2
Vol. of $CrCl_2$	= 1.85	3.7
Strength	= 0.2703 N	0.2703 N

(Vide curve No. 62)

Titrations in presence of HCl:

Table LXXV.

5 c.c. $CuSO_4$ + 5 c.c. HCl + 20 c.c. H_2O

Strength of HCl = 0.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.308	
0.5 c.c.	-0.096	
1.02 "	-0.095	
1.5 "	-0.100	
1.7 "	-0.098	1
1.8 "	-0.077	21
1.9 "	-0.025	52
2.0 "	-0.034	9
2.1 "	-0.038	
3.0 "	-0.044	
3.5 "	-0.009	
3.6 "	0.001	10
3.7 "	0.049	50
3.8 "	0.181	132
4.2 "	0.215	8.5

Break	1	2
Vol. of $CrCl_2$ =	1.85	3.75
Strength =	0.2703 N	0.2667 N

(Vide curve No. 63)

Table LXXVI

5 c.c. $CuSO_4$ + 10 c.c. HCl + 15 c.c. H_2O

Strength of HCl = 1.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.329	
0.51 c.c.	-0.102	
1.0 "	-0.090	
1.5 "	-0.091	
1.7 "	-0.082	4.5
1.8 "	-0.069	13
1.9 "	0.002	71
2.0 "	0.010	10
2.5 "	-0.024	
3.0 "	-0.025	
3.5 "	0.003	
3.6 "	0.021	18
3.7 "	0.035	14
3.79 "	0.146	123
4.0 "	0.182	15

Break	1	2
Vol. of $CrCl_2$ =	1.85	3.75
Strength =	0.2703 N	0.2667 N

(Vide curve No. 64)

TABLE LXXVII

5 c.c. $CuSO_4$ + 20 c.c. HCl
+ 5 c.c. H_2O

Strength of HCl = 2.0 N

Vol of $CrCl_2$	Potential	ΔE/ Δc
-	-0.335	
0.5 c.c.	-0.107	
1.02 "	-0.100	
1.5 "	-0.096	
1.7 "	-0.082	7
1.81 "	-0.071	10
1.9 "	0.052	21
2.0 "	0.025	27
2.5 "	-0.010	7
3.0 "	-0.008	
3.5 "	0.019	
3.6 "	0.028	
3.7 "	0.045	17
3.8 "	0.165	120
4.0 "	0.192	13.5

Break	1	2
Vol. of $CrCl_2$ =	1.88	3.8
Strength =	0.2667 N	0.263 N

(Vide curve No. 65)

Titrations in presence of KCl.

TABLEL LXXVIII

5 c.c. $CuSO_4$ + 5 c.c. KCl
+ 20 c.c. H_2O

Strength of Kcl = 0.5 N

Vol. of $CrCl_2$	Potential	ΔE/ Δc
-	-0.212	
0.5 c.c.	-0.046	
1.0 "	-0.050	
1.5 "	-0.048	
1.7 "	-0.037	6
1.8 "	-0.010	27
1.9 "	-0.005	6.6
2.0 "	-0.003	
3.01 "	-0.015	
3.5 "	0.005	
3.6 "	0.018	13
3.7 "	0.249	231
3.8 "	0.271	22
4.01 "	0.282	

Break	1	2
Vol. of $CrCl_2$ =	1.8	3.7
Strength =	0.2777 N	0.2703 N

(Vide curve No. 66)

TABLE LXXIX.

5 c.c. $CuSO_4$ + 10 c.c. KCl
+ 15 c.c. H_2O

Strength of KCl = 100 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.245	
0.5 c.c.	-0.071	
1.0 "	-0.074	
1.5 "	-0.070	
1.69 "	-0.064	
1.8 "	-0.045	8.2
1.85 "	0.008	106
1.9 "	-0.007	30
2.0 "	-0.020	
3.0 "	-0.025	
3.5 "	0.000	
3.59 "	0.016	17.8
3.7 "	0.225	190
3.8 "	0.251	26
4.0 "	0.269	

Break	1	2
Vol. of $CrCl_2$	1.85	3.7
Strength =	0.2703 N	0.2703 N

(Vide curve No. 67)

TABLE LXXX.

5c.c. $CuSO_4$ + 20 c.c. KCl
+ 5 c.c. H_2O

Strength of KCl = 2.0 N

Vol. of $CrCl_2$	Potential	ΔE/Δc
-	-0.257	
0.5 c.c.	-0.082	
1.0 "	-0.073	
1.49 "	-0.075	
1.7 "	-0.064	5
1.8 "	-0.054	19
1.85 "	0.021	15
2.0 "	0.000	14
3.0 "	-0.026	
3.5 "	-0.010	
3.6 "	-0.001	
3.69 "	0.011	
3.8 "	0.049	42
4.0 "	0.224	87.5
4.5 "	0.250	5.2

Break	1	2
Vol. of $CrCl_2$ =	1.85	3.85
Strength =	0.2703 N	0.2597 N

(Vide curve No.68)

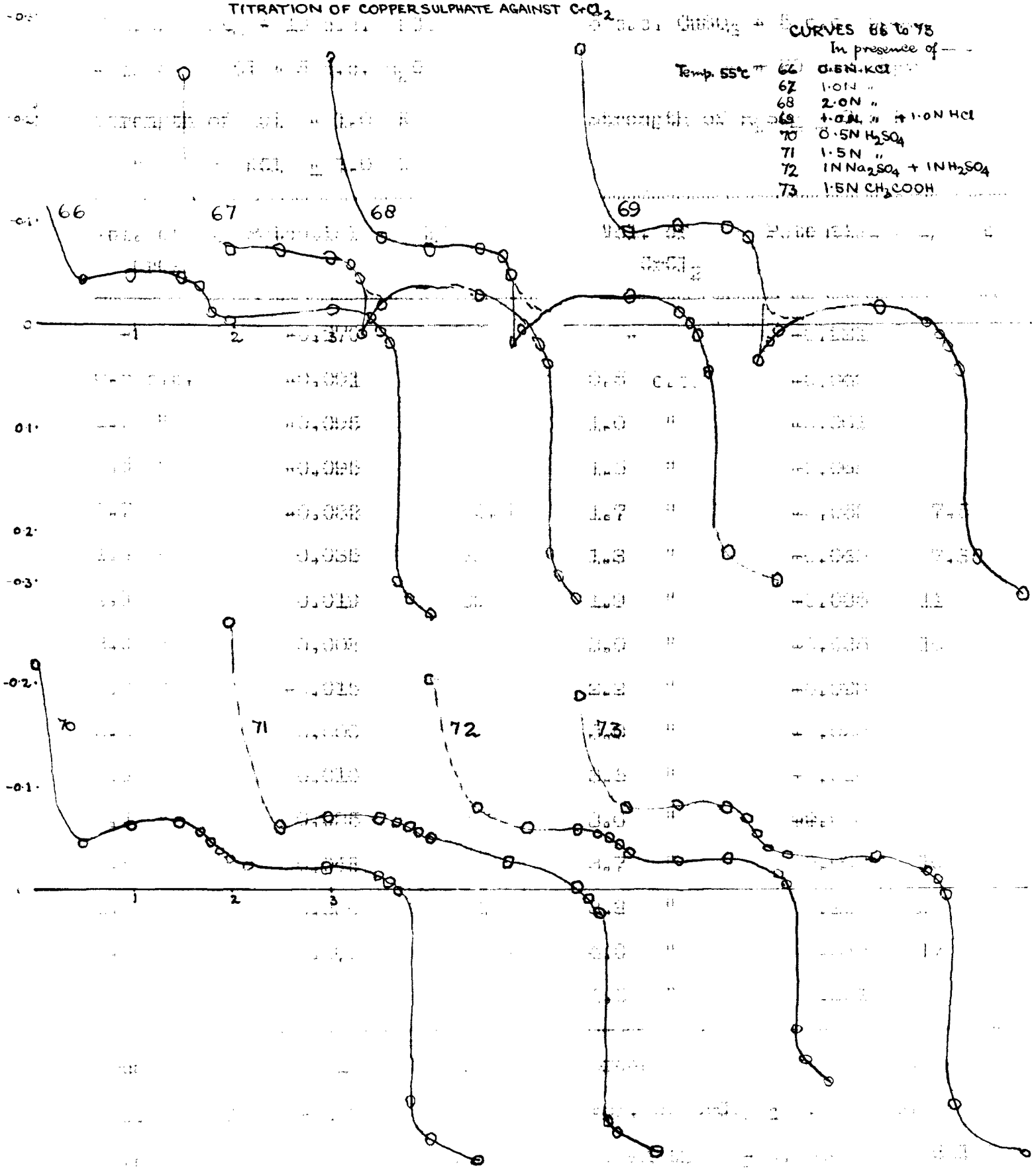
TITRATION OF COPPER SULPHATE AGAINST $CrCl_2$

CURVES 66 to 73

In presence of —

Temp. 55°C

66 0·5N·KCl
67 1·0N "
68 2·0N "
69 1·0N " + 1·0N HCl
70 0·5N H_2SO_4
71 1·5N "
72 1N Na_2SO_4 + 1N H_2SO_4
73 1·5N CH_3COOH



Titration in presence of Na_2SO_4 & H_2SO_4

TABLE LXXXIII

5 c.c. $CuSO_4$ + 15 c.c. H_2SO_4 + 10 c.c. H_2O

Strength of H_2SO_4 = 1.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.260	
0.5 c.c.	-0.061	
1.0 "	-0.073	
1.5 "	-0.070	
1.7 "	-0.065	
1.8 "	-0.061	4
1.9 "	-0.056	5
2.0 "	-0.050	6
2.8 "	-0.023	
3.5 "	0.001	
3.6 "	0.012	
3.7 "	0.025	13
3.8 "	0.224	199
3.9 "	00240	26
4.3 "	0.255	

Break	1	2
Vol. of $CrCl_2$ =	-	3-75
Strength =	-	0.2667 N

(Vide curve No. 71)

TABLE LXXXIV

5 c.c. $CuSO_4$ + 10 c.c. H_2SO_4 + 10 c.c. Na_2SO_4 + 5 c.c. H_2O

Strength of H_2SO_4 = 1.0 N

" " Na_2SO_4 = 1.0 N

Vol of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.202	
0.5 c.c.	-0.078	
1.0 "	-0.061	
1.5 "	-0.060	
1.7 "	-0.051	
1.8 "	-0.048	3.3
1.9 "	-0.041	7
2.0 "	-0.036	5
2.5 "	-0.027	
3.0 "	-0.026	
3.5 "	-0.011	
3.6 "	-0.002	9
3.7 "	0.140	142
3.8 "	0.171	31
4.0 "	0.192	

Break	1	2
Vol. of $CrCl_2$ =	(2.0)	3.70
Strength =	0.2500 N	0.2703 N

(Vide curve No. 72)

Titration in presence of KCl & HCl.

TABLE LXXXI

5 c.c. $CuSO_4$ + 10 c.c. HCl
+ 10 c.c. KCl + 5 c.c. H_2O

Strength of HCl = 1.0 N
" " KCl = 1.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.270	
0.5 c.c.	-0.091	
1.0 "	-0.095	
1.5 "	-0.095	
1.7 "	-0.082	6.5
1.8 "	0.035	78
1.9 "	0.019	32
2.0 "	0.008	
3.0 "	-0.015	
3.5 "	0.000	
3.6 "	0.010	
3.7 "	0.025	15
3.8 "	0.048	23
4.0 "	0.230	91
4.5 "	0.263	6.5

Break	1	2
Vol. of $CrCl_2$	= 1.85	3.9
Strength	= 0.2703 N	0.2564 N

(Vide curve No. 69)

Titrations in presence of H_2SO_4

TABLE LXXXII

5 c.c. $CuSO_4$ + 5 c.c. H_2SO_4
+ 20 c.c. H_2O

Strength of H_2SO_4 = 0.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.221	
0.5 c.c.	-0.046	
1.0 "	-0.061	
1.5 "	-0.068	
1.7 "	-0.053	7.5
1.8 "	-0.045	7.3
1.9 "	-0.035	11
2.0 "	-0.025	10
2.2 "	-0.023	
3.0 "	-0.020	
3.5 "	-0.016	
3.6 "	-0.008	
3.7 "	0.002	10
3.8 "	0.210	190
4.0 "	0.245	17
4.5 "	0.261	

Break	1	2
Vol. of $CrCl_2$	= 1.95	3.8
Strength	= 0.2564 N	0.2631 N

(Vide curve No. 70)

Titration in presence of HAc

TABLE LXXXV

5 c.c. $CuSO_4$ + 15 c.c. HAc + 10 c,c. H_2O

Strength of HAc = 1.5 N

Vol. of $CrCl_2$	Potential	ΔE/ Δc
-	-0.191	
0.5 c.c.	-0.075	
1.0 "	-0.079	
1.5 "	-0.076	
1.7 "	-0.068	4
1.8 "	-0.052	16
1.9 "	-0.039	13
2.0 "	-0.030	
3.0 "	-0.029	
3.6 "	-0.016	
3.6 "	0.008	
3.7 "	0.010	18
3.8 "	0.213	203
4.5 "	0.260	7

Break	1	2
Vol. of $CrCl_2$	=(2.85)	3.75
Strength	= 0.2703 N	0.2667 N

(Vide table No.73)

Titrations in presence of KCl & HAc

TABLE LXXXVI

5 c.c. $CuSO_4$ + 5 c.c. KCl + 10 c.c. HAc + 10 c.c. H_2O

Strength of KCl = 0.5 N

" " HAc = 1.0 N

Vol. of $CrCl_2$	Potential	ΔE/ Δc
-	-0.264	
0-5 c.c.	-0.095	
1.02 "	-0.083	
1.5 "	-0.080	
1.7 "	-0.071	4.3
1.8 "	-0.046	25
1.9 "	-0.024	22
2,1 "	-0.018	
3.0 "	-0.029	
3.5 "	-0.020	
3.6 "	-0.012	7.3
3.7 "	0.221	259
3.8 "	0.265	44
4.0 "	0.277	
4.5 "	0.281	

Break	1	2
Vol. of $CrCl_2$	= 1.83	3.70
Strength	= 0.2732 N	0.2703 N

(Vide table No. 74)

TABLE LXXXVII

5 c.c. $CaSO_4$ + 10 c.c. KCl + 10 c.c. HAc + 5 c.c. H_2O

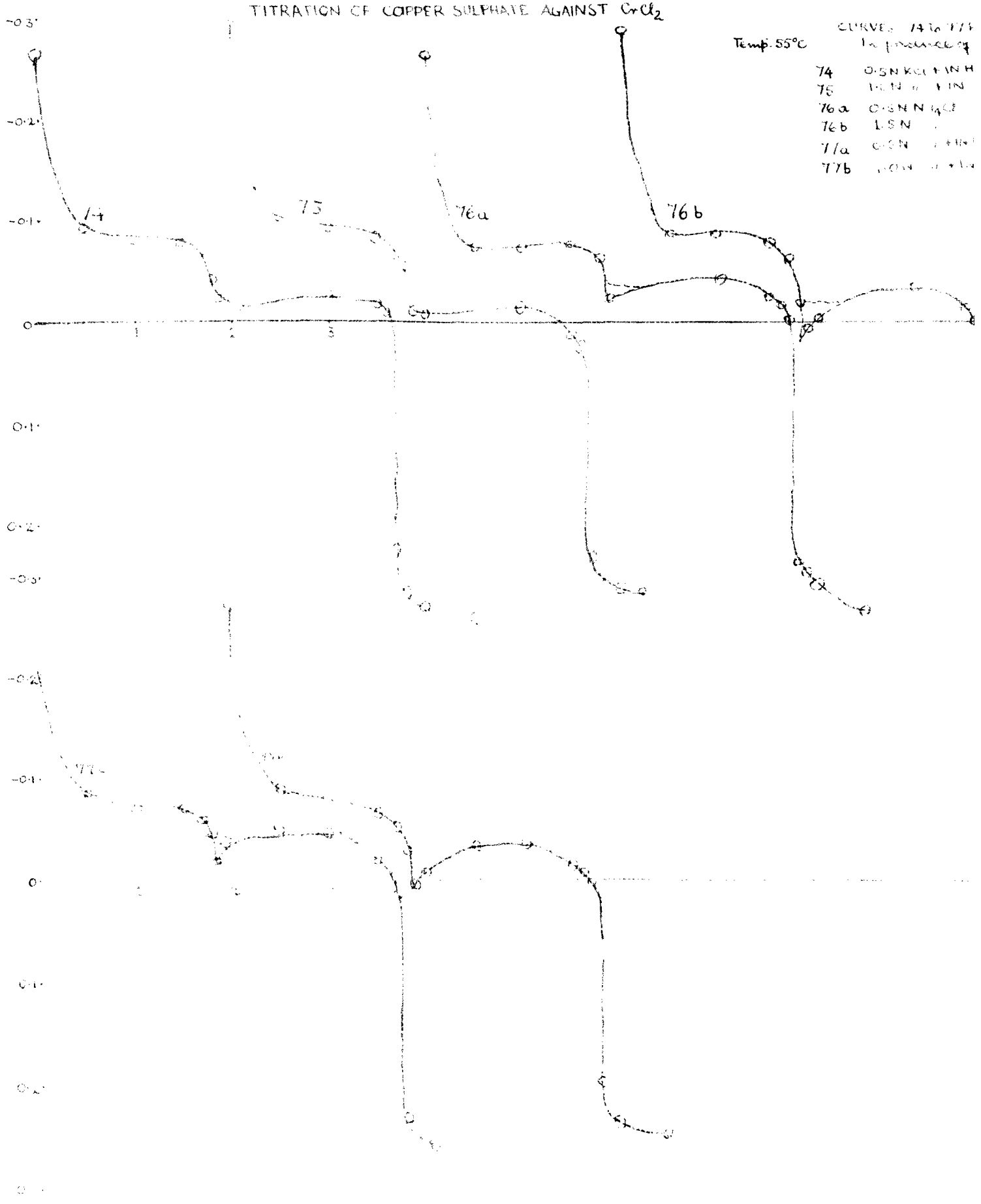
Strength of KCl. = 1.0 N

Strength of HAc = 1.0 N

Vol. of $CaCl_2$	Potential	$\Delta E/\Delta c$
-	+0.296	
0.5 c.c.	+0.104	
1.0 "	+0.096	
1.5 "	+0.084	
1.7 "	+0.070	7
1.8 "	+0.050	11
1.9 "	+0.013	50
2.0 "	+0.010	3
3.0 "	+0.016	
3.5 "	+0.010	
3.6 "	+0.023	13
3.7 "	0.231	208
3.79 "	0.250	21
4.0 "	0.259	
4.2 "	0.262	
636		

Break	1	2
Volume of $CaCl_2$	= 1.83	3.65
Strength	= 0.2732 N	0.2720 N

(Wolfe Curve No. 75)


TITRATION OF COPPER SULPHATE AGAINST $CrCl_2$
Temp. 55°C
74
75
76a
76b
77a
77b

Titrations in presence of ammonium chloride:

TABLE LXXXVIII

5 c.c. $CuSO_4$ + 5 c.c. NH_4Cl + 20 c.c. H_2O

Strength of NH_4Cl = 0.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.266	
0.5 c.c.	-0.078	
0.99 "	-0.077	
1.5 "	-0.080	
1.7 "	-0.074	
1.8 "	-0.073	1
1.89 "	-0.024	54.4
2.0 "	-0.030	55
3.0 "	-0.046	
3.5 "	-0.027	
3.6 "	-0.018	
3.7 "	-0.004	14
3.8 "	-0.231	235
4.0 "	0.254	11.5
4.5 "	0.285	

Break	1	2
Vol. of $CrCl_2$	1-85	3.75
Strength	0.2703 N	0.2667 N

(Vide curve No..764)

TABLE LXXXIX

5 c.c. $CuSO_4$ + 15 c.c. NH_4Cl + 20 c.c. H_2O

Strength of NH_4Cl = 1.5 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	-0.288	
0.5 c.c.	-0.090	
1.0 "	-0.086	
1.5 "	-0.081	
1.7 "	-0.063	9.4
1.8 "	-0.020	43
1.9 "	+0.005	25
2.01 "	-0.004	
3.0 "	-0.033	
3.5 "	-0.016	
3.6 "	-0.001	
3.7 "	0.032	30
3.8 "	0.215	183
4.0 "	0.238	11.5

Break	1	2
Vol. of $CrCl_2$	1.83	3.8
Strength	0.2732 N	0.2631 N

Vide curve No. 766)

Titrations in presence of HAc and NH_4Cl.

[illegible] KCl.	[illegible] KCl.
5 c.c. $CrSO_4$ + 5 c.c. NH_4Cl	5 c.c. $CrSO_4$ + 10 c.c. NH_4Cl
+10 c.c. HAc + 10 c.c. H_2O	+10 c.c. HAc + 5 c.c. H_2O
Strength of NH_4Cl :: 0.5 N	Strength of NH_4Cl :: 1.0 N
" " HAc :: 1.0 N	" " HAc :: 1.0 N

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	+0.373	
0.5 c.c.	+0.084	
1.0 "	+0.073	
1.5 "	+0.071	
1.7 "	+0.036	
1.8 "	+0.047	17.3
1.85 "	+0.018	72
2.0 "	+0.004	[illegible]
2.5 "	+0.051	
3.0 "	+0.049	
3.5 "	+0.033	
3.6 "	+0.010	
3.7 "	0.016	22
3.8 "	0.232	242
4.0 "	0.231	95

Break	1	2
Vol. of $CrCl_2$ ::	1.85	3.75
Strength ::	0.3703 N	0.2337 N

(Vide curve No. 77a)

Vol. of $CrCl_2$	Potential	$\Delta E/\Delta c$
-	+0.274	
0.5 c.c.	+0.000	
1.0 "	-0.031	
1.5 "	+0.054	
1.7 "	-0.050	7
1.8 "	+0.031	19
1.9 "	0.004	36
1.95 "	+0.005	17
2.5 "	+0.038	
3.0 "	+0.032	
3.5 "	-0.015	
3.6 "	+0.000	
3.7 "	0.001	10
3.8 "	0.201	200
4.0 "	0.240	19.5
4.5 "	0.252	

Break	1	2
Vol. of $CrCl_2$ ::	1.93	3.8
Strength ::	0.2702 N	0.2331 N

(Vide curve No. 77b)

My results on the effect of acids, salts and their mixtures on the titration carried out between copper sulphate and chromous chloride are summarised in the following table:

T A B L E XCII

Table No.	Reagent	Concentration of the reagent	Strength of $CrCl_2$ from 1st Break	Strength of $CrCl_2$ from 2nd Break	Nature of the curves* 1st break	Nature of the curves* 2nd break
Temperature 25°C						
28	Water	-	0.2858	0.2739	F.S.	S.
29	HCl	0.1 N	0.2809	0.2739	S.F.	S.
30	"	0.2 N	0.2777	0.2688	F.S.	S.
31	"	0.5 N	0.2739	0.2667	S.	S.
32	"	1.0 N	0.2739	0.2667	S.	S.
33	"	1.5 N	0.2732	0.2631	S.	S.F.
34	"	2.0 N	0.2748	0.2631	S.	S.F.
35	KCl	0.1 N	0.2809	0.2777	F.	S.
36	"	0.2 N	0.2809	0.2739	F.S.	S.
37	"	0.5 N	0.2777	0.2681	S.	S.
38	"	1.0 N	0.2777	0.2667	S.	S.
39	"	1.5 N	0.2732	0.2631	S.	S.
40	"	2.0 N	0.2777	0.2631	S.	S.F.
41	H_2SO_4	0.1 N	0.2703	0.2739	Q.F.	F.S.
42	"	0.2 N	0.2732	0.2739	Q.F.	S.
43	"	0.5 N	(0.2703)	0.2703	Q.F.	S.
44	"	1.0 N	(0.2631)	0.2688	Q.F.	S.
45	"	1.5 N	(0.2703)	0.2703	Q.F.	S.
46	"	2.0 N	(0.2631)	0.2681	Q.F.	S.
47	Na_2SO_4	0.1 N	(0.2631)	0.2717	F.	S.
48	"	0.2 N	(0.2564)	0.2703	F.	S.
49	"	0.5 N	-	0.2703	Q.F.	S.
50	"	1.0 N	-	0.2717	Q.F.	S.
51	"	1.5 N	-	0.2703	Q.F.	S.
52	HAc	0.1 N	(0.2631)	0.2703	F.S.	S.
53	"	0.2 N	(0.2576)	0.2688	F.S.	S.
54	"	0.5 N	(0.2564)	0.2717	F.	S.
55	"	1.0 N	-	0.2703	Q.F.	S.
56	"	1.5 N	(0.2631)	0.2688	Q.F.	S.
57	"	2.0 N	-	0.2717	Q.F.	F.S.
58	NaAc	0.1 N	-	(0.2597)	Q.F.	F.
59	"	0.2 N	-	-	Q.F.	Q.F.
60	KCl-HCl	KCl 0.1N, HCl	0.1N, 0.2858	0.2739	F.S.	S.
61	"	" 1.0N, "	0.1N, 0.2748	0.2667	S.	S.
62	"	" 0.1N, "	1.0N, 0.2732	0.2667	Q.S.	S.
63	"	" 1.0N, "	1.0N, 0.2748	0.2631	Q.S.	S.

Contd.

Table No.	Reagent	Concentration of the reagent	Strength of $CrCl_2$ from 1st break	Strength of $CrCl_2$ from 2nd break	Nature of the curves* 1st break	Nature of the curves* 2nd break
Temperature 25°C.						
64	H_2SO_4 - Na_2SO_4	0.1 N, 0.1 N	0.2631	0.2703	F.	S.
65	" "	0.1 N, 1.0 N	0.2564	0.2739	Q.F.	S.
66	" "	1.0 N, 0.1 N	(0.2564)	0.2739	Q.F.	S.
67	" "	1.0 N, 0.75N	-	-	Q.F.	F.
68	HAc - NaAc	0.1 N, 0.1 N	0.2564	0.2703	Q.F.	S.
69	" "	1.0 N, 0.1 N	-	(0.2667)	Q.F.	F.
70	KCl - HAc	0.1 N, 0.1 N	0.2631	0.2703	S.	S.
71	" "	1.5 N, 0.5 N	0.2739	0.2631	S.	S.
72	" "	0.5 N, 1.5 N	0.2703	0.2667	S.	S.
73	" "	1.0 N, 100 N	0.2703	0.2564	S.	F.S.
Temperature 55°C.						
74	(water)	- -	0.2703	0.2703	F.	S.
75	HCl	0.5 N	0.2703	0.2667	S.	S.
76	"	1.0 N	0.2703	0.2667	S,	S.
77	"	2.0 N	0.2868	0.2630	S.	S.
78	KCl	0.5 N	0.2777	0.2703	F.	S.
79	"	1.0 N	0.2703	0.2703	F.S.	S.
80	"	2.0 N	0.2703	0.2597	F.S.	F.S.
81	KCl - HCl	1.0 N, 1.0 N	0.2703	0.2564	Q.S.	F.S.
82	H_2SO_4	0.5 N	(0.2564)	0.2631	Q.F.	S.
83	"	1.5 N	-	0.2667	Q.F.	S.
84	H_2SO_4 - Na_2SO_4	1.0 N. 1.0 N	(0.2500)	0.2703	F.	F.
85	HAc	1.5 N	(0.2703)	0.2667	F.	F.
86	KCl - HAc	0.5 N, 1.0 N	0.2732	0.2703	S.	S.
87	" "	1.0 N, 1.0 N	0.2732	0.2739	Q.S.	S.
88	NH_4Cl	0.5 N	0.2703	0.2667	S.	S.
89	"	1.5 N	0.2782	0.2631	S.	F.
90	NH_4Cl - HAc	0.5 N, 1.0 N	0.2703	0.2667	F.	S.
91	" "	1.0 N, 1.0 N	0.2732	0.2631	F.	S.

* F. - Flat; S. - Sharp; Q.F.- Quite Flat; Q.S. - Quite Sharp; S.F.- Slightly Flat; F.S. - Fairly Sharp

Discussion:

Copper sulphate solution is usually recommended for the estimation of chromous ions. The following conclusions have been arrived at by carrying out titrations of chromous chloride against standard copper sulphate solution in presence of acids and their salts, and at higher temperature.

From the summarised table (No. 92) as well as from the curves(vide curves Nos. 76 to 77) it may be seen that all though the second break (where Cu(ii) is reduced to Cu)is pronounced in majority of cases, sharp break in the first stage is observed in presence of HCl, KCl or a mixture of HCl and KCl. At higher concentrations of HCl or KCl the seperation of cuprous chloride is not observed and in these cases quite sharp breaks at the first stage (Cu(ii) ——Cu(i)) of reduction are obtained. With H_2SO_4 the second break is fairly sharp but with Na_2SO_4 or a mixture of Na_2SO_4 and H_2SO_4 typical titration curves are not obtained. From the large number of experiments it was found that although the chloride ions (may be from KCl or NH_4Cl) are competent enough to give typical titration curves (with two breaks), the presence of acids (hydrogen ions) is highly desireable since it allows a steady value quickly after the addition of small quantities of the titrant.

The equilibrium potentials expected at the two stages of reduction (0.1075 V and -0.0765 V) are not realised in any case. This however does not affect the determination of the strength of the solution. Results coinciding with the values obtained by other methods (0.2739 N) are achieved by considering the second stage reduction for lower concentrations of HCl or KCl or both while

higher concentrations of these electrolytes give such concordant values even from the first break. As for other electrolytes only in a few scattered cases (lower concentrations of H_2SO_4 and Na_2SO_4 HAc and KCl at the first stage, KCl and HAc at a high temperature NH_4Cl at a high temperature and NH_4Cl and HAc), values approximating the real concentration of chromous chloride could be obtained. The titrations at higher temperatures give values lower than the actual concentration of chromous chloride. The only advantage of carrying out experiments at a higher temperature is that the equilibrium is attained easily (i.e. the steady potential is realised soon after the addition of the titratnt).

Since the reaction Cr(ii) + Cu(ii) $\rightleftharpoons$ Cu(i) + Cr(iii) involves two unstable ions the necessary conditions for carrying out the titration is to keep both of them in stable form while carrying out the reaction. This can only be achieved when complexing agents are present, and preferably sufficient H^+ ions to check their hydrolysis are present together with complexing anions. The purpose cannot be achieved by taking complexing agents like citrate tartrate or oxalate or corresponding acids since,as shown earlier they give precipitates or complexes with strong ligands which, although, stabilise the lower valency state of both Cu and Cr, do not give free ions for the reaction. This would result in giving flat curves from which the strength of chromous chloride cannot be determined.

From the extensive study of these titrations it is found that the conditions laid down by Zintl and Rienacker(loc cit) for using chromous chloride as an analytic al reagent need

modifications. It is to be observed that neither the presence of excess of chloride nor higher temperature is necessary for obtaining good results. On the contrary excess of Cl' ions help in realising the first break in a more striking manner than when lower concentration of the ion isused. Also lower values for the concentration of chromous chloride are obtained on carrying out titrations at high temperatures.

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CHAPTER IV.

POLAROGRAPHIC STUDY OF VARIOUS SAMPLES OF Cr(iii), AND Cr(ii):

It has been seen from potential measurements that the normal potential (E_o) of a chromous-chromic system is dependent on factors like the concentration of the solution, the presence of H^+ and other foreign ions and above all on the electrode used. Also the different varieties of chromic chloride, when added to the solution or formed during its oxidation, seemed to influence the redox potential values (vide chapter II). Some such observations, therefore, suggested the necessity of investigating the behaviour of chromous and chromic ions at the dropping mercury electrode.

M.Demassieux and J.Heyrovsky[1] in 1929 studied the polarography of Cr(iii). The polarograms showed breaks in the curve at 0.7 V. and 1.35 V. indicating that the electro-chemical reduction of Cr(iii) takes place in two stages:

1. $Cr^{+++} + 1\,e \longrightarrow Cr^{++}$,

2. $Cr^{+++} + 3\,e \longrightarrow Cr$.

They observed that the addition of acid does not exert any effect on the deposition potential showing that H^+ ions do not enter into electrolytic process which may be thus expressed entirely by the reaction $Cr^{+++} + 1\,e \longrightarrow Cr^{++}$. The deviation potential from the theoretical values suggested that it was easier to reduce the green complex $CrCl_2(H_2O)_4\ Cl \cdot 2\,H_2O$ than the violet form $Cr(H_2O)_6\ Cl_3$ which predominates in dilute solutions. The reduction of various chromic alums were also studied by these authors and found that the curves for alums showed a

more abrupt rise than those for chlorides or sulphate. This was explained by asuming that an imperfect equilibrium existed between the green and the violet modifications.

The polarography of isomeric chromium sulphate was studied by J.D.WILLIS[2] and he observed two steps, the first at -1.041 V. (vs. s.c.e.) which did not change with dilution. The second merged with H discharge step at 0.02 M solution or higher concentration. The green chromium sulphate under goes irreversible reduction. He also observed that the violet alum changed to green on heating and showed a polarogram similar to that of green chromic sulphate.

Later in 1949 Ingane and Pecsok[3] studied the hydrolysis current of chromic ion. From a systematic investigation of the polarographic behaviour of Cr(iii) ion in KCl and $NaClO_4$ solutions they found that the optimum conditions for well defined doublet wave was (1) a concentration of supporting electrolyte of 0.1 M or less (2) the natural p_H(about4) resulting from the hydrolysis of Cr(iii) and (3) a concentration of 0.005 to 0.01 % gelatin as maximum suppressor.

While the first wave was directly proportional to concentration, the second was relatively too large and increased with increasing concentration. This excess current resulted from the simultaneous reduction of H^+ion , a product of hydrolysis. The above authors[4] also studied the polarographic behaviour of chromium (iii) in supporting electrolytes containing KCl, $CaCl_2$, SCN , Citrate, [illegible], oxalate, acetate, lactate, succinate, and salicylate ions, ammonia buffers, and $NaNH_4Br$ and Et_4NI .

A reversible oxidation of Cr^{++} ion and a nearly reversible reduction of Cr^{+++} occured in saturated $CaCl_2$ at -0.51 (vs. s.c.e.) The SCN^- complex was irreversibly oxidised with E/2 of -0.85 V., this potential being a function of SCN^- concentration. They could not observe any complex formation in weak acids and the waves were similar to that in KCl. At higher p_H, the oxidation wave was displaced negatively and the half wave potential of the different complexes of Cr(ii) was taken as a measure of their reducing power. The half wave potentials varied with different electrolyte and their concentration. A few of their results are summarised below:-

Supporting electrolyte	E/2 Vs. s.c.e.	$i_{lim} 2/t^{1/2}$
0.1 M KCl	- .34	-1.54
1.0 M KCl	- .40	-1.54
Sat. KCl	- .51	-1.55
Sat. $CaCl_2$	- .51	-0.57
0.05 M KCNS	- .71	-1.55
0.5 M KCNS	- .78	-1.78
1.0 M KCNS	- .80	-1.64
0.1 M NH_4OH 5 M NH_4Cl	- .85	-1.14
0.5 M HCOOH	- .30	-1.54
0.1 M $(CH_3)_4N.Br.$	- .43	-1.54

Lingane and Kerlinger[5] found that Cr(iii) ions form a stable complex in an M/10 pyridine - M/10 pyridinium chloride which reduces to chromous state and producing a step with E/2 - 0.95. A half wave potential of -1.0 V. was observed for Cr^{+++} in saturated tataric acid[6], probably due to reduction of chromic tatarate.

From the above it is evident that just as the potentiometric determination of the electrode potential of the chromous-chromic system depends on various factors like p_H of the medium,

presence of foreign ions, the nature and stability of the oxidised form of Cr(iii), electrode material etc. , the polarographic determination of E/2 also depends on many such factors. Hence, in support of my observations from the potentiometric studies with the chromous solution prepared by the reduction of green chromic chloride with zinc and hydrochloric acid it was thought worth while to carry out some polarographic studies on different varieties of Cr(iii) and Cr(ii) under identical conditions. This chapter, deals with my investigation on the cathodic reduction of the violet and green (both freshly prepared and aged [illegible] of the solution). Varieties of chromic chloride and that of the sample obtained by the oxidation of chromous chloride. E/2 for the cathodic wave of different solutions of chromous chloride during its successive oxidation have also been determined. The experiments were carried out in presence of different supporting electrolytes of varying concentrations.

EXPERIMENTAL.

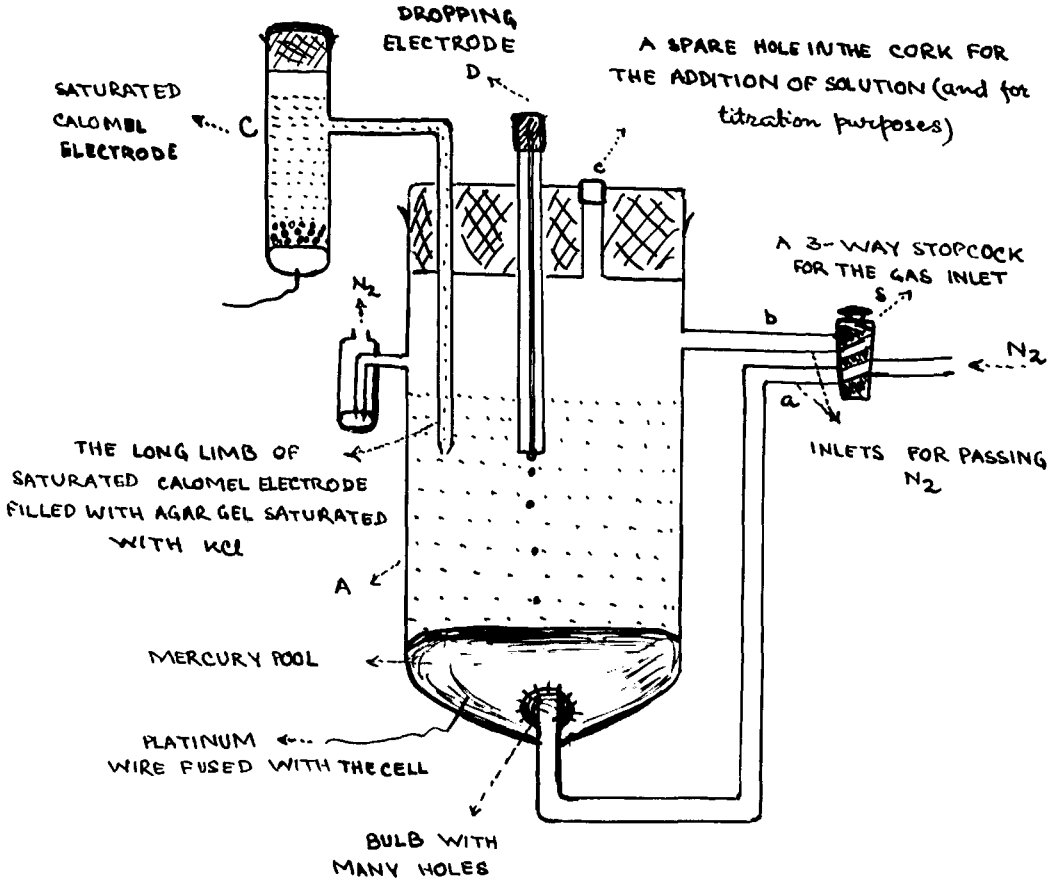
I. Reduction of different varieties of chromic chloride at the dropping mercury electrode.

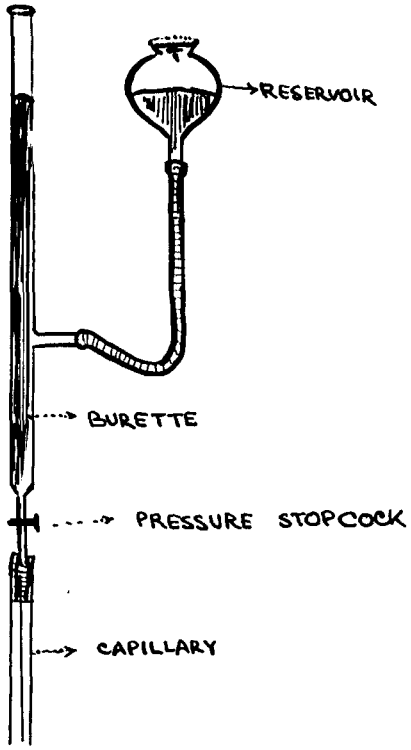
A. The apparatus and techniques used:

A Fischer Electropode was used for the experiments. A Multiflex galvanimeter type MGF-2 was used as the external current measuring device in order to get a wide range of sensitivity and easy manipulation. Polarographic cells and calomel electrodes were prepared in the laboratory, to suit the purpose. Commercial nitrogen purified by passing through washers containing ammoniacal cuprous chloride, chromous chloride and water successively, was used for deaeration and keeping the inert atmosphere through out the experiments .

The polarographic cell of the type shown in fig 5 was prepared from pyrex glass tube of three cm. diameter. Two gas inlet tubes A and B served for deaeration and for keeping the inert atmosphere during the experiment respectively; a being provided with a bulb B having many holes for easy deaeration, a and b are joined to a three way stop cock s which is opened to"a" for deaeration and to "b" while taking readings. A platinum wire P was fused to the bottom of the cell to be used while taking readings with the mercury pool as the anode. The cell was fitted with the air tight rubber cork provided with three holes for dropping electrode, for calomel electrode and the third open hole C used to transfer solutions (or for the nozzle of the burette when titrations were carried out) and which was kept closed while not in use.

FIG. 5





A.... POLAROGRAPHIC CELL OF 50 C.C. CAPACITY

A catch O with mercury seal served as the outlet for nitrogeh. The saturated calomel electrode C was provided with a long side limb L which served as a bridge. A boiling test tube was used for making the calomel electrode. The side tube L (bridge) of C C was filled with agar gel saturated with pure KCl. (This electrode was found to serve most satisfactorily and hence the Beckmann fibre type calomel electrode used in my preliminary experiments was replaced).

The capillary of the dropping electrode D was connected to a constant pressure head burette arrangement by neoprene tubing so that the drop time could easily be controlled.

Preparation of agar gel and calomel electrode:

The gel for the bridge (side limb of calomel electrode) was prepared by adding 100 c.c. of cold water to 3-3.5 gm of pure agar and heating over a water bath, stirring till a homogeneous solution was obtained. 25 gm of solid KCl was then added to it and the solution was stirred untill the salt dissolved. The side limb of the tube was then filled with this fluid by suction and then allowed to cool when an effective gel - KCl bridge was obtained. The calomel electrode was then prepared using redistilled mercury, and A. R. KCl and "Calomel" and kept aside at least for six hours before use. The side limb "L" was always kept in saturated KCl solution when not in use.

Preparation of gelatine solution:

Freshly prepared gelatine solution was used as maxima suppressor in all my experiments. A 0.1 % solution was prepared by

treating 0.1 gm of pure granulated gelatine with 100 c.c. of double distilled water and finally heating on the steam bath with thorough stirring until dissolution was complete. A concentration of 0.005 % of gelatine was used for all the experiments. This was adjusted by adding the requisite amount of the sample in the polarographic cell.(Usually 1.5 c.c. of the gelatine added and total volume made up to 30.0 c.c.). Concentrations higher than what is actually required to suppress the maxima have generally deleterious influence on the wave[7,8]. A solution prepared in this way was not used for more than two daysAas decomposed gelatine influences the wave characteristics.

Preparation of the reagents:

A decimolar solution of chromic chloride (250 c.c.) was prepared from the sample of the green hydrate by dissolving the calculated amount in double distilled water. (Double distilled water was prepared using an all glass pyrex distillation apparatus for the use of all the experiments on polarography). Aged solution when required was obtained by keeping this solution for one month. By this time the solution turned violet in colour. The exact concentration of the solution was then determined potentiometrically as described in Chapter,I page 16.

The fresh solution of chromic chloride (0.1 M) was prepared whenever required and was not used for more than a day.

A pure violet variety of chromic chloride was prepared as described in chapter, II, page 34 and an exactly 0.1 M solution of the sample prepared. A pure sample of chromic chloride completely free from any traces of mine or acetic acid was also prepared and a part of it (the rest was stored and used for experimental [illegible] with potassium [illegible]). Adjusted by

atmospheric oxygen. The chromium content of this solu
determined by oxidising 2.0 c.c. of it to chromate and
potentiometrically against ferrous ammonium sulphate in
acid medium. An exactly decimolar solution was then prepared out of
this sample by dilution to the calculated extent with water.

All the other reagents required were prepared from A.R. samples by dissolving the calculated amounts indouble distilled water.

Procedure:-

Reduction of various samples of chromic chloride;

The polarographic waves of the four samples of chromic chloride were first of all taken with three different concentrations (1.0, 2.5 and 5 m.molar) of chromic chloride and supporting electrolyte, potassium chloride(0.1M, .5 M and 2 M). A concentration of 0.005 % gelatine was used in each case. All readings were taken against saturated calomel electrode. The drop time was maintained constant(3.2 - 3.4 sec) throughout the experiment by adjusting the height of the mercury column. The galvanometer deflections(proportional to current) were recorded in the following tables. the sensitivity of the galvanometer was kept constant throughout (1:10 position) and only the sensitivity of the electropode was adjusted whenever required.

Blank readings with supporting electrolyte and gelatine were always taken before every new set of experiment to make the correction for residual current, and also to make sure of the complete deaeration by nitrogen.

Fresh Green Solution.

T A B L E XCIII.

Vol. of 0.1 M $CrCl_2$ used	= 0.5 c.c.
Total volume made up	= 20.0 c.c.
Volume of 2 M KCl	= 1.0 c.c.
Drop time (at 1.0 Volt)	= 3.2 sec
Gelatine percentage	= 0.005 %
Sensitivity	= 20 X
Conc. of Cr(iii)	= 2.5 m.moles
Conc. of KCl	= 0.1 M

	Potential applied (in volts)	Galv. readings (in m.m.)
1	0.1	-0.5
2	0.2	-0.5
3	0.3	-0.25
4	0.4	-0.25
5	0.5	-0.00
6	0.6	0.5
7	0.7	2.5
8	0.8	4.5
9	0.9	6.5
10	1.0	8.0
11	1.1	9.5
12	1.2	10.0
13	1.3	10.0
14	1.4	10.5
15	1.5	10.5
16	1.6	20.0
17	1.7	30.0
18	1.8	30.2
19	1.9	30.5
20	2.0	30.5

(Vide Curve No 78)

TABLE XCIV.

Concentration of Cr(iii) = 2.5 m.moles
Concentration of KCl = 0.5 N
Drop time = 3.2 sec.
Sensitivity = 20 X

Potential applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.2
0.3	0.0
0.4	0.0
0.5	0.2
0.6	0.5
0.7	1.5
0.8	3.5
0.9	6.0
1.0	8.5
1.1	9.5
1.2	9.8
1.3	10.0
1.4	10.0
1.5	11.0
1.6	25.5
1.7	29.5
1.8	30.0
1.9	30.5
1.98	42.5

(Vide curve No. 79)

TABLE XCV.

Conc. of Cr(iii) = 2.5 m.moles
Conc. of KCl = 2.0 N
Drop time = 3.25 sec.
Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.5
0.3	-0.2
0.4	0.0
0.5	0.2
0.6	1.0
0.7	2.8
0.8	5.0
0.9	7.0
1.0	8.5
1.1	9.5
1.2	10.0
1.3	10.2
1.4	11.0
1.5	13.2
1.6	28.0
1,7	30.0
1.8	30.0
1.9	30.5
2.0	40.5

(Vide curve No,80)

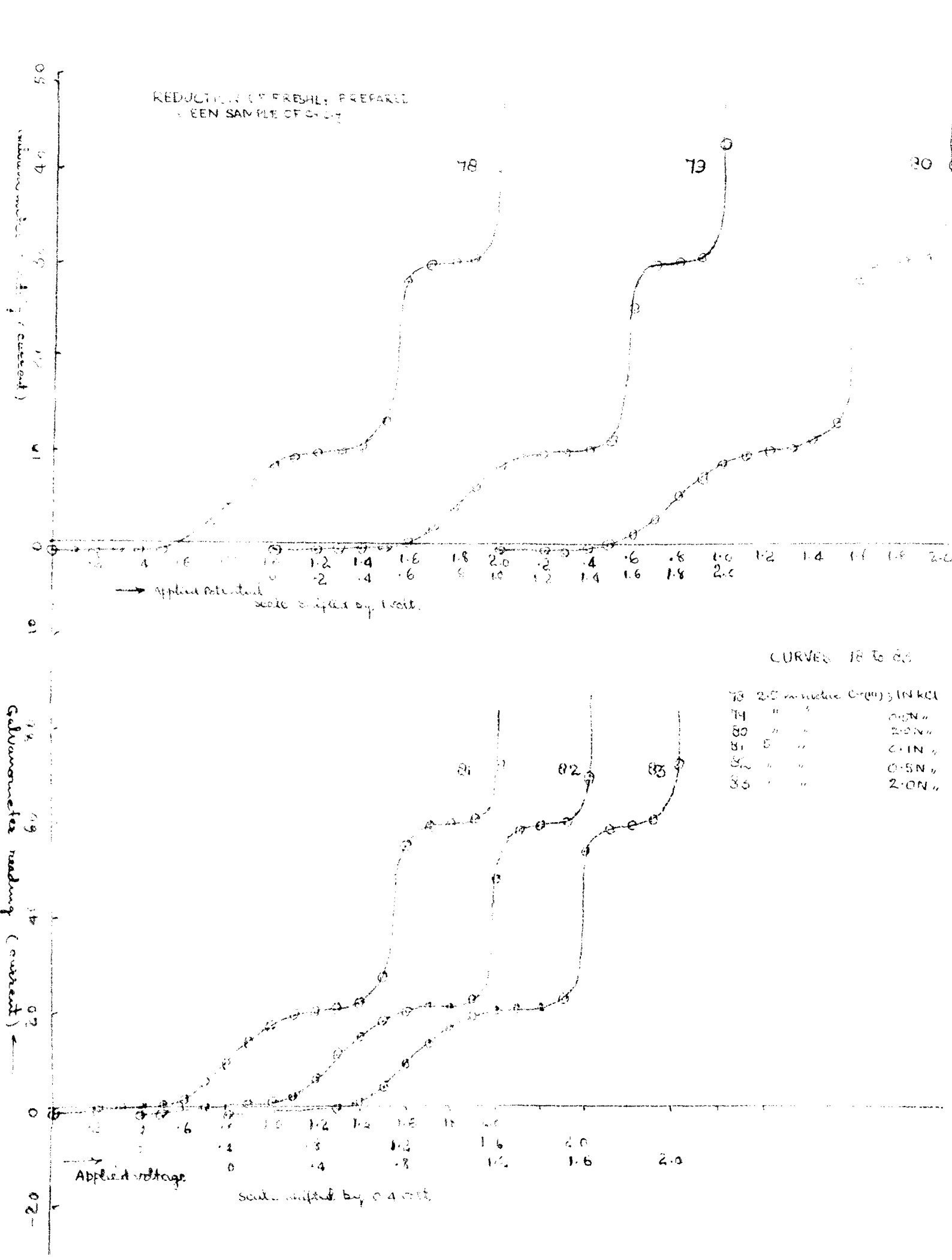

REDUCTION OF FRESHLY PREPARED
EEN SAMPLE OF
78
79
80
Galvanometer reading (current)
Applied potential
Scale shifted by 1 volt.
CURVES 78 to 85
78 2·0 N solution of
79 1·0 N "
80 0·5 N "
81 0·2 N "
82 0·1 N "
83 0·05 N "
81
82
83
Galvanometer reading (current)
Applied voltage
Scale shifted by 0·4 volt.

TABLE XCVI

Conc. of Cr(iii) = 5 m.moles
Conc. of KCl = 0.1 N
Drop time = 3.2 sec.
Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.2
0.3	0.0
0.4	0.0
0.5	000
0.6	1.2
0.7	5.0
0.8	9.0
0.9	13.5
1.0	17.0
1.1	18.0
1.2	20.0
1.3	20.2
1.4	20.5
1.5	28.0
1.6	55.0
1.7	60.0
1.8	60.5
1.9	61.0
1.99	73.0

(Vide curve No. 81)

TABLE XCVII

Conc. of Cr(iii) = 5 m.moles
Conc. of KCl = 0.5 N
Drop time = 3.2 sec.
Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-1.0
0.2	-0.5
0.3	-0.2
0.4	-0.2
0.5	0.0
0.6	0.0
0.7	1.5
0.8	5.0
0.9	9.5
1.0	14.5
1.1	17.0
1.2	20.0
1.3	20.0
1.4	20.0
1.5	22.0
1.6	48.0
1.7	59.0
1.8	60.0
1.9	60.5
1.98	69.0

(Vide curve No, 82)

TABLE XCVIII

Conc. of Cr(iii) = 5 m.moles

Conc, of KCl = 2 N

Drop time = 3.15 sec.

Sensitivity = 20 X

Pot. Applied (in volts)	Galv. readings (in m.m.)
0.1	-1.0
0.2	-0.5
0.3	0.0
0.4	0.0
0.5	0.2
0.6	1.0
0.7	4.0
0.8	8.0
0.9	13.0
1.0	15.5
1.1	18.0
1.2	20.0
1.3	20.0
1.4	20.5
1.5	22.5
1.6	55.0
1.7	59.0
1.8	60.0
1.9	61.0
1.98	74.0

(Vide curve No. 83)

TABLE XCIX

Conc. of Cr(iii) =1 m.mole

Conc. of KCl =0.1 N

Drop time =3.2 sec.

Sensitivity =50 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.5
0.3	-0.2
0.4	0.0
0.5	0.0
0.6	1.0
0.7	3.5
0.8	7.0
0.9	9.5
1.0	11.0
1.1	12.5
1.2	12.8
1.3	12.8
1.4	13.0
1.5	14.5
1.6	40.0
1.7	44.5
1.8	45.0
1.98	48.0

'Vide curve No,84)

TABLE C

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.5 N

Drop time = 3. 2 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.5
0.3	-0.2
0.4	0.0
0.5	0.0
0.6	1.0
0.7	3.0
0.8	7.0
0.9	8.5
1.0	10.2
1.1	11.0
1.2	12.5
1.3	12.5
1.4	13.0
1.5	15.0
1.6	35.0
1.7	44.0
1.8	45.0
1.9	45.5
1.98	47.5

(Vide curve No. 85)

TABLE CI

Conc. of Cr(iii) = 1 m. mole

Conc. of KCl = 2 N

Drop time = 3.25 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-0.5
0.3	-0.2
0.4	0.0
0.5	0.5
0.6	1.0
0.7	3.0
0.8	5.5
0.9	8.5
1.0	10.0
1.1	11.5
1.2	12.5
1.3	12.5
1.4	13.0
1.5	14.5
1.6	42.0
1.7	45.5
1.8	46.0
1.9	46.5
1.99	52.0

(Vide curve No. 86)

84
95
Applied voltage
87
88

Readings with Green solution aged:

TABLE CII

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.2 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.0
0.4	0.2
0.5	0.2
0.6	0.2
0.7	0.6
0.8	0.5
0.9	2.5
1.0	9.0
1.1	12.0
1.2	12.5
1.3	13.0
1.4	13.0
1.5	15.0
1.6	43.5
1.7	46.5
1.8	47.0
1.9	47.0
1.99	50.5

(Vide curve No. 87)

TABLE CIII

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.5 N

Drop time = 3.1 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.5
0.7	1.0
0.8	1.0
0.9	2.5
0.95	5.0
1.0	9.0
1.1	12.5
1.2	13.0
1.3	13.0
1.4	13.5
1.5	15.2
1.6	45.0
1.7	47.0
1.8	47.5
1.9	47.5
1.98	50.0

(Vide curve No. 88)

TABLE CIV

Conc. of Cr(iii). = 1 m.mole

Conc. of KCl = 2 N

Drop time = 3.2 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.2
0.4	0.5
0.5	0.5
0.6	1.0
0.7	1.0
0.8	1.5
0.9	3.5
1.0	11.0
1.1	13.0
1.2	13.5
1.3	13.5
1.4	14.0
1.5	15.5
1.6	46.5
1.7	48.5
1.8	48.5
1.9	49.0
1.98	62.0

(Vide curve No. 89)

TABLE CV

Conc. of Cr(iii) = 2.5 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.1 sec

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.0
0.4	0.2
0.5	0.2
0.6	0.2
0.7	0.5
0.8	1.5
0.9	6.0
1.0	17.0
1.1	19.5
1.2	20.0
1.3	20.0
1.4	20.5
1.5	26.0
1.6	58.0
1.7	60.0
1.8	60.0
1.9	663.0
1.98	80.0

(Vide curve No. 90)

TABLE CVI

Conc. of Cr(iii) = 2.5 m.mole

Conc. of KCl = 0.5 N

Drop time = 3.3 sec.

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.0
0.4	0.0
0.5	0.5
0.6	0.5
0.7	0.5
0.8	1.0
0.9	4.0
1.0	15.0
1.1	19.0
1.2	20.0
1.3	20.0
1.4	20.5
1.5	28.0
1.6	57.0
1.7	61.0
1.8	61.0
1.9	61.5
1.98	75.0

(Vide curve No.91)

TABLE CVII

Conc. of Cr(iii) = 2.5 m.mole

Conc. of KCl = 2.0 N

Drop time = 3.2 sec.

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.0
0.7	1.0
0.8	1.5
0.9	3.5
1.0	15.5
1.1	20.0
1.2	20.0
1.3	20.5
1.4	21.0
1.5	25.5
1.6	59.0
1.7	61.0
1.8	61.0
1.9	62.5
1.98	74.5

(Vide curve No. 92)

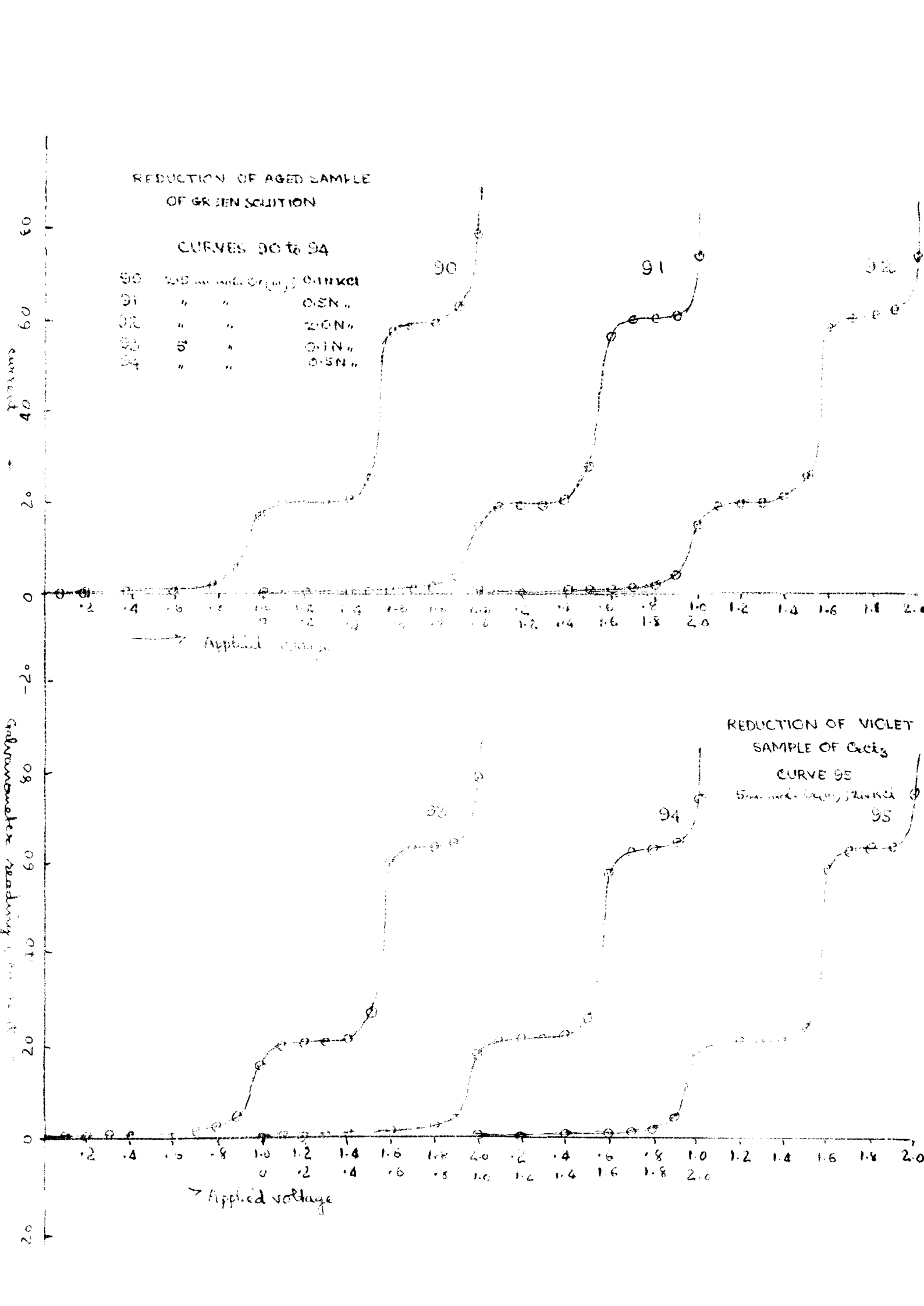

REDUCTION OF AGED SAMPLE
OF GREEN SOLUTION
CURVES 90 to 94
90 0·1N KCl
91 " " 0·5N "
92 " " 2·0N "
93 " " 0·1N "
94 " " 0·5N "
90
91
92
93
94
95
Galvanometer reading
Applied voltage
REDUCTION OF VIOLET
SAMPLE OF CrCl3
CURVE 95
0·1N KCl

TABLE CVIII

Conc. of Cr(iii) = 5 m.moles

Conc. of KCl = 0.1 N

Drop time = 3.2 sec.

Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.5
0.4	0.5
0.5	0.5
0.6	1.0
0.7	1.0
0.8	2.0
0.9	5.0
1.0	16.5
1.1	21.0
1.2	21.0
1.3	21.0
1.4	21.5
1.5	27.0
1.6	60.5
1.7	64.0
1.8	64.5
1.9	64.5
2.0	79.0

(Vide curve No. 93)

TABLE CVIX

Conc. of Cr(iii) = 5 m.moles

Conc. of KCl = 0.5 N

Drop time = 3.15 sec.

Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.5
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.0
0.7	1.5
0.8	2.0
0.9	4.5
1.0	19.0
1.1	21.0
1.2	21.5
1.3	21.5
1.4	22.5
1.5	26.5
1.6	59.0
1.7	63.0
1.8	64.0
1.9	64.5
1.99	76.0

Vide curve No. 94)

Readings with violet sample:

TABLE CX

Conc. of Cr(iii) = 5 m.mole

Conc. of KCl = 2 N

Drop time = 3.3 sec.

Sensitivity = 20 X

POT. APPLIED (in volt)	GALV. READINGS (in m.m.)
A 0.1	0.0
0.2	0.5
0.3	0.5
0.4	1.0
0.5	1.0
0.6	1.5
0.7	1.5
0.8	2.0
0.9	5.0
1.0	19.0
1.1	21.0
1.2	21.5
1.3	21.0
1.4	21.5
1.5	24.5
1.6	60.0
1.7	63.0
1.8	64.0
1.9	64.0
1.98	77.0

(Vide curve No. 95)

TABLE CXI

Conc. of Cr(iii) = 5 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.2 sec.

Sensitivity = 20 X

POT. APPLIED (in volt)	GALV. READINGS (in m.m.)
0.1	0.0
0.2	0.5
0.3	0.5
0.4	1.0
0.5	1.5
0.6	2.0
0.7	2.0
0.8	2.0
0.9	4.0
1.0	13.0
1.1	21.0
1.2	21.0
1.3	21.5
1.4	21.5
1.5	24.0
1.6	67.5
1.7	64.0
1.8	65.0
1.9	65.0
1.99	79.0

(Vide curve No. 96)

TABLE CXII

Conc. of Ur(iii) = 5 m.mole

Conc, of KCl = 0.5 N

Drop time = 3.1 sec

Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
U	
0.1	0.0
0.2	0.2
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.5
0.7	1.5
0.8	2.0
0.9	4.0
1.0	12.5
1.1	20.5
1.2	21.0
1.3	21.5
1.4	22.5
1.5	24.5
1.6	60.0
1.7	63.5
1.8	65.0
1.9	65.5
1.99	75.0

(Vide curve No.97)

TABLE CXIII

Conc. of Cr(iii) = 5 m.mole

Conc. of KCl = 2 N

Drop time = 3.1 sec.

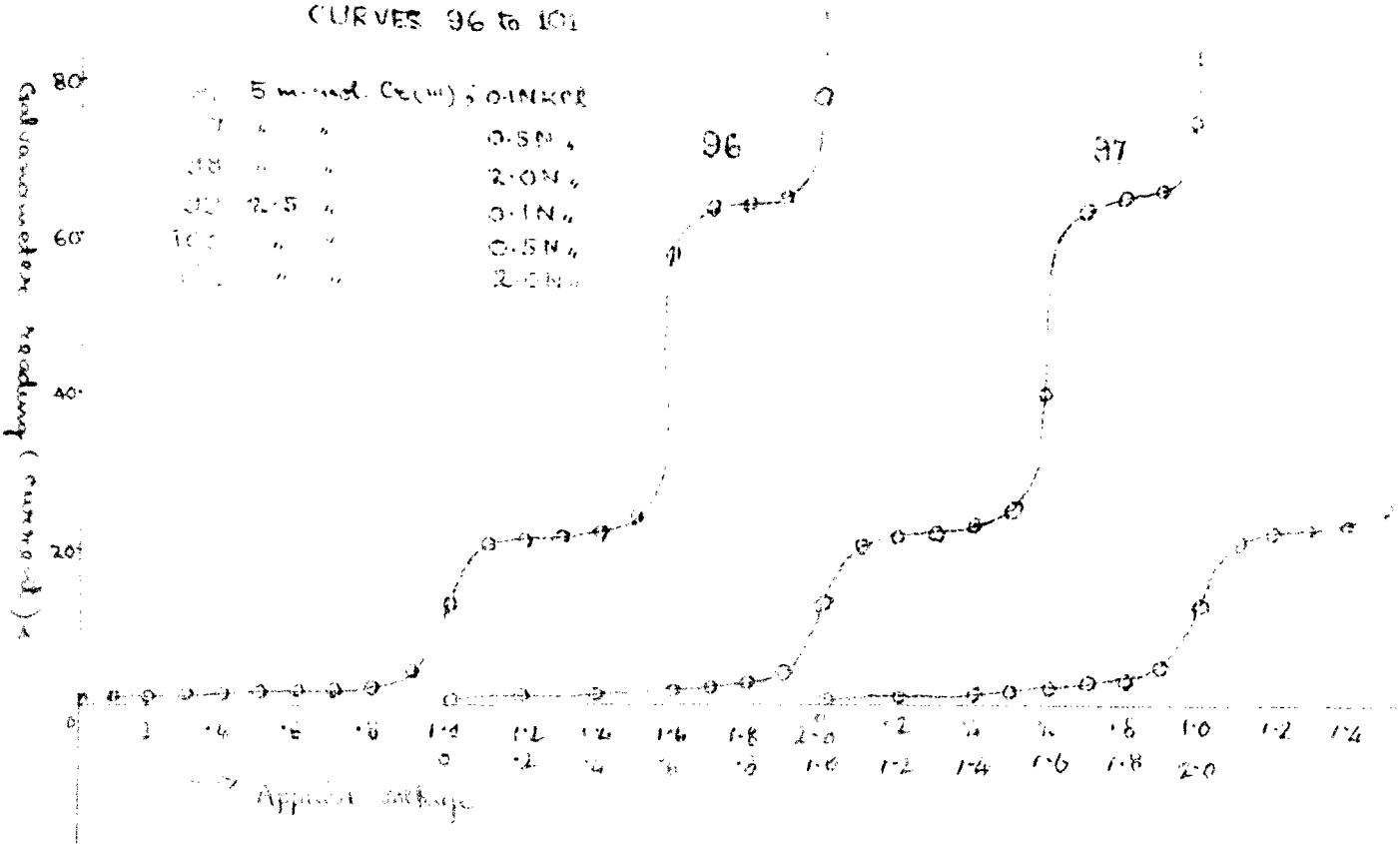
Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.5
0.3	0.5
0.4	1.0
0.5	1.0
0.6	1.5
0.7	1.5
0.8	2.0
0.9	5.0
1.0	12.5
1.1	20.5
1.2	21.5
1.3	22.0
1.4	22.5
1.5	25.0
1.6	60.0
1.7	65.0
1.8	66.0
1.9	66.5
1.98	77.0

(Vide curve No. 98)

REDUCTION OF VIOLET SAMPLE OF [illegible]

CURVES 96 to 101



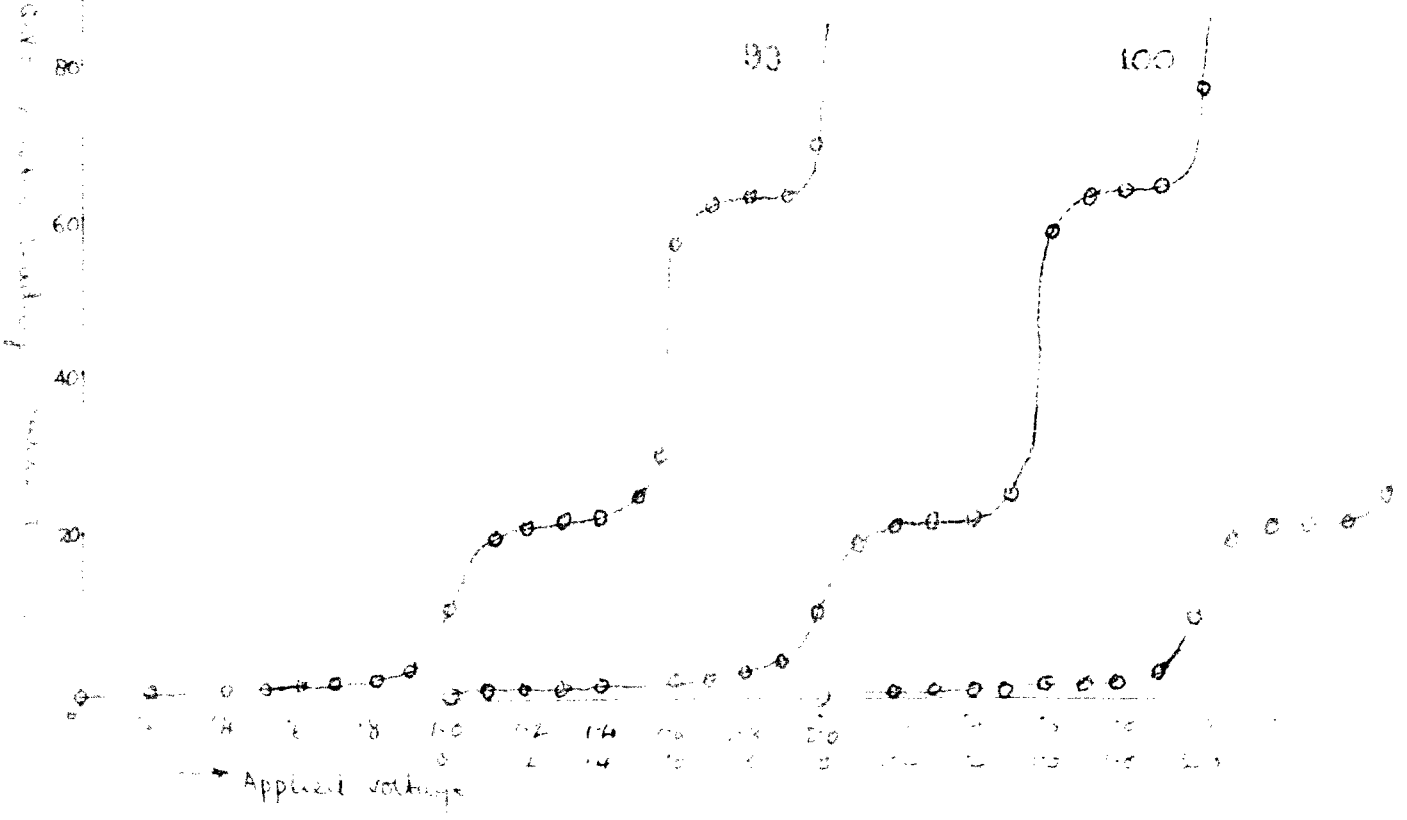


TABLE CXIV

Conc. of Cr(iii) = 2.5 M.Mole

Conc. of KCl = 1.0 N

Droptime = 1.2 sec.

Sensitivity = 10X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.0
0.7	1.5
0.8	2.0
0.9	3.5
1.0	10.0
1.1	19.5
1.2	20.5
1.3	21.0
1.4	21.0
1.5	24.5
1.6	56.5
1.7	61.5
1.8	62.0
1.9	62.0
1.95	65.0

(Vide curve No. 99)

TABLE CXV

Conc. of Cr(iii) = 2.5 M.Mole

Conc. of KCl = 0.5 N

Drop time = 3.1 sec.

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.5
0.7	1.5
0.8	2.5
0.9	4.0
1.0	10.0
1.1	19.0
1.2	21.0
1.3	21.5
1.4	22.0
1.5	25.0
1.6	60.0
1.7	63.0
1.8	64.0
1.9	64.0
1.98	79.0

(Vide curve No. 100)

TABLE CXVI

Conc. of Cr(iii) = 2.5 n.mole.

Conc. KCl = 2.0 N

Drop time = 3.2 sec.

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.5
0.3	0.5
0.4	0.5
0.5	1.0
0.6	1.5
0.7	2.0
0.8	2.0
0.9	3.5
1.0	10.0
1.1	20.5
1.2	21.0
1.3	21.0
1.4	21.0
1.5	25.0
1.6	62.0
1.7	65.0
1.8	65.0
1.9	67.0
1.98	80.0

(vide curve No. 101)

TABLE CXVII

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.2 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	0.0
0.2	0.5
0.3	0.5
0.4	0.5
0.5	0.5
0.6	0.5
0.7	0.8
0.8	1.0
0.9	2.0
1.0	7.5
1.1	13.0
1.2	13.0
1.3	13.2
1.4	13.5
1.5	15.5
1.6	42.5
1.7	44.0
1.8	44.0
1.9	44.5
1.99	50.2

(Vide curve No. 102)

TABLE CXVIII

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.5 N

Drop time = 3.2 sec.

Sensitivity = 5 X

Pot. applied (in volts)	galv. readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.2
0.4	0.2
0.5	0.5
0.6	1.0
0.7	1.2
0.8	1.5
0.9	3.0
1.0	9.0
1.1	12.5
1.2	13.0
1.3	13.0
1.4	13.5
1.5	16.5
1.6	40.0
1.7	43.5
1.8	44.5
1.9	44.5
1.98	47.5

(vide curve No. 103)

TABLE CXIX

Conc. of Cr(iii) = 1 m.mole

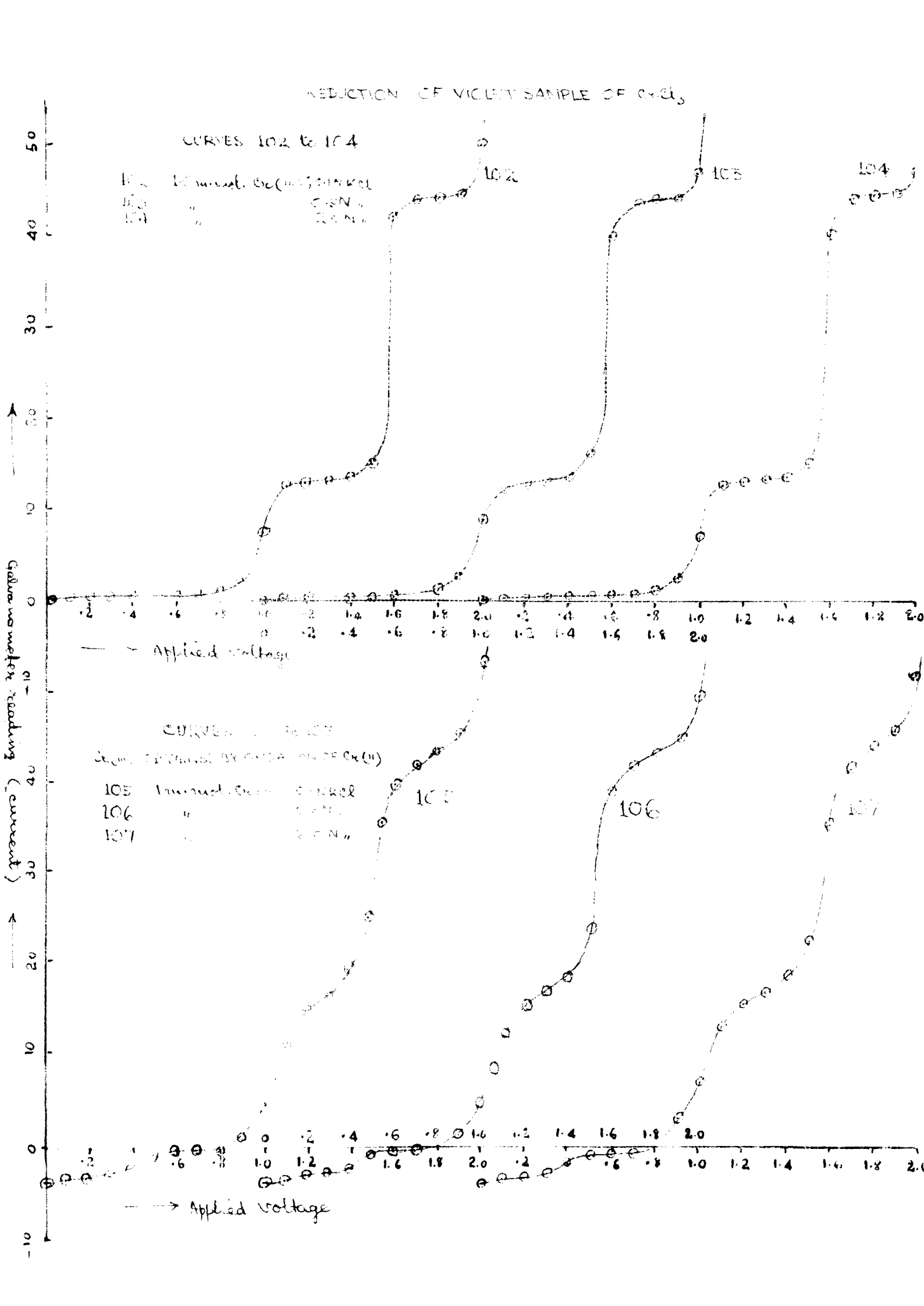
Conc. of KCl = 2.0 N

Drop time = 3.1 sec

Sensitivity = 5 X

Pot. applied (in volts)	galv readings (in m.m.)
0.1	0.0
0.2	0.0
0.3	0.2
0.4	0.2
0.5	0.5
0.6	0.5
0.7	0.5
0.8	1.0
0.9	2.5
1.0	7.0
1.1	12.5
1.2	13.0
1.3	13.5
1.4	13.5
1.5	15.0
1.6	40.0
1.7	44.5
1.8	44.5
1.9	45.0
1.99	48.0

(Vide curve No 104)


REDUCTION OF VIOLET SAMPLE OF Cr·Cl3
CURVES 102 to 104
102
103
104
Galvanometer reading (current)
Applied voltage
CURVES
105
106
107
105
106
107
Galvanometer reading (current)
Applied voltage

Readings with Cr(iii) solution obtained by atmospheric oxidation of chromous chloride

TABLE CXX

Conc. of Cr(iii) = 1 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.3.sec

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-0.5
0.2	-3.0
0.3	-3.0
0.4	-2.5
0.5	-0.5
0.6	-0.2
0.7	0.0
0.8	0.0
0.9	1.0
1.0	4.0
1.1	10.5
1.2	14.5
1.3	16.0
1.4	19.0
1.5	25.0
1.6	40.0
1.7	42.0
1.8	43.5
1.9	45.5
1.99	53.5

(vide curve No. 105)

TABLE CXXI

Conc, of Cr(iii) = 1 m.mole

Conc . of KCl = 0.5 N

Drop time = 3.25 sec .

Sensitivity = 5 X

Pot applied (in volts)	Galv. readings (in m.m.)
0.1	-3.5
0.2	-3.0
0.3	-2.5
0.4	-2.0
0.5	-0.5
0.6	0.0
0.7	0.0
0.8	0.5
0.9	1.0
1.0	5.0
1.1	12.0
1.2	15.5
1.3	17.0
1.4	18.5
1.5	23.5
1.6	39.5
1.7	42.0
1.8	43.5
1.9	45.0
1.98	50.6

(vide curve No. 106)

[illegible]	[illegible]
Conc. of Cr(III) = 1.0 m. mole	Conc. of Cr(III) = 2.0 m. mol
[illegible] = 2 N	Conc. of KCl = 3.1 N
Drop time = 3.4 sec.	Drop time = 3.1 sec.
Conductivity = 5 m.A	Conductivity = 14 m.A

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-3.5
0.2	-3.0
0.3	-2.5
0.4	-1.5
0.5	-0.5
0.6	-0.5
0.7	-[illegible]
0.8	0.5
0.9	3.0
1.0	7.0
1.1	13.0
1.2	15.5
1.3	17.0
1.4	18.5
1.5	22.5
1.6	30.0
1.7	42.0
1.8	54.0
1.9	65.5
1.90	83.5

(Vide curve No. 27)

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-10.0
0.2	-10.0
0.3	- 9.5
0.4	- 1.0
0.5	- 5.5
0.6	- 3.0
0.7	-1 .0
0.8	0.0
0.9	4.0
1.0	12.0
1.1	20.0
1.2	23.5
1.3	23.0
1.4	27.0
1.5	33.0
1.6	44.0
1.7	61.0
1.8	67.0
1.9	73.5
1.9.	8[illegible].0

(Vide curve No. 28)

TABLE CXXIV

Conc. of Cr(iii) = 2.5 m.mole

Conc. of KCl = 0.5 N

Drop time = 3.2 sec.

Sensitivity = 10 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-9.5
0.2	-9.5
0.3	-9.0
0.4	-9.0
0.5	-4.0
0.6	-2.0
0.7	-1.0
0.8	0.0
0.9	4.0
1.0	12.5
1.1	20.0
1.2	23.5
1.3	25.0
1.4	28.0
1.5	35.0
1.6	48.0
1.7	59.0
1.8	65.0
1.9	70.5
1.98	80.0

(Vide curve No. 109)

TABLE CXXV

Conc. of Cr(iii) = 2.5 m.mole

Conc. of KCl = 2.0 N

Drop time = 3.2 sec.

Sensitivity = 10 X

Pot applied (in volts)	Galv. readings (in m.m.)
0.1	-8.5
0.2	-8.5
0.3	-8.0
0.4	-6.0
0.5	-3.0
0.6	-2.5
0.7	-1.5
0.8	0.0
0.9	4.5
1.0	10.0
1.1	20.5
1.2	25.0
1.3	27.5
1.4	31.5
1.5	36.5
1.6	52.0
1.7	65.0
1.8	72.0
1.9	77.5
1.99	85.5

(Vide curve No. 110)

REDUCTION OF VIOLET SAMPLE OF $CrCl_3$

CURVES 108 to 112 b

108
109
110
111
112a
112 b

0·5N.
2·0N.

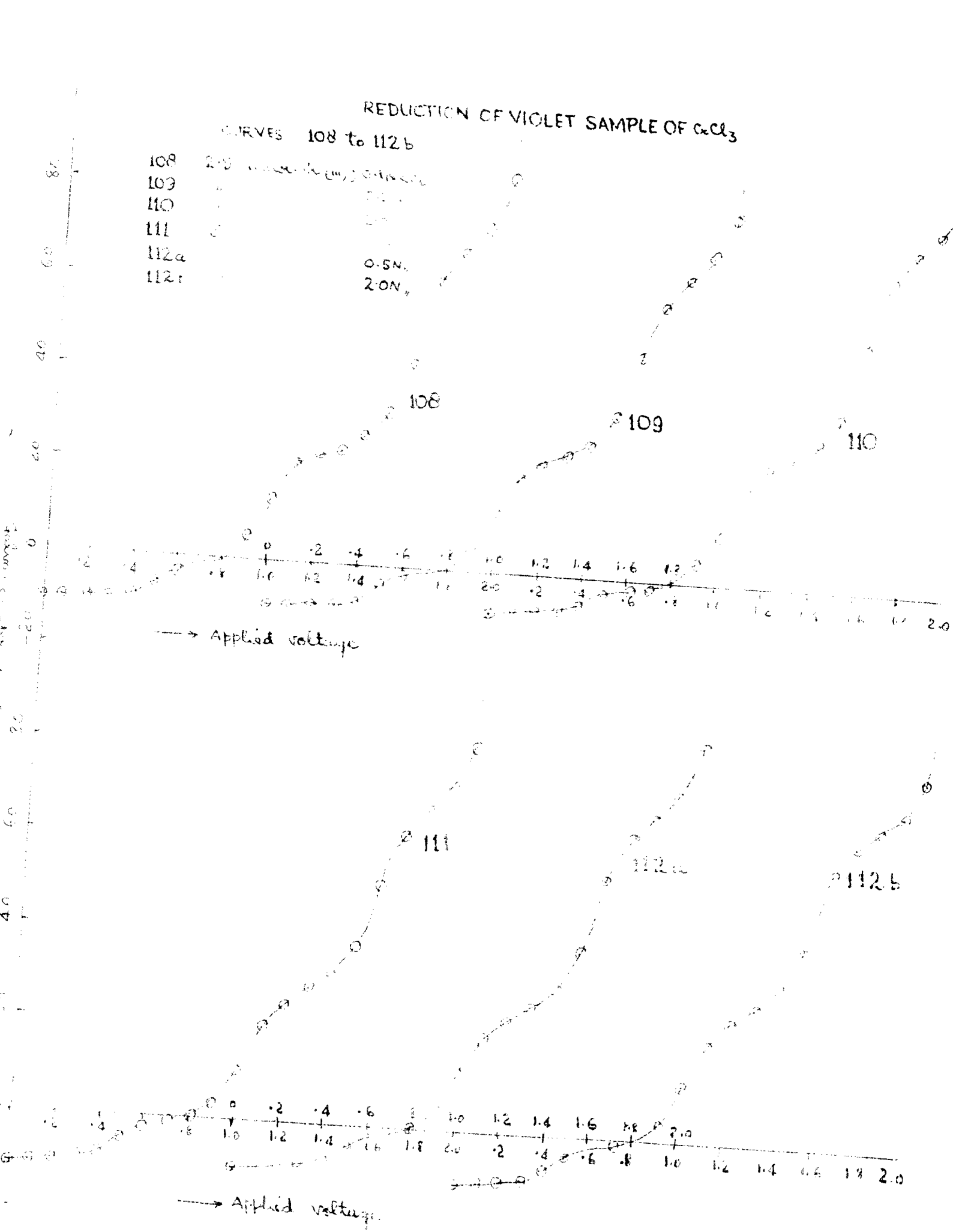


TABLE CXXVI

Conc. of Cr(iii) = 5 m.mole

Conc. of KCl = 0.1 N

Drop time = 3.1 sec.

Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-10.5
0.2	-10.0
0.3	- 9.5
0.4	- 8.5
0.5	- 5.0
0.6	-2 .0
0.7	- 1.5
0.8	0.0
0.9	3.0
1.0	10.0
1.1	19.5
1.2	24.5
1.3	28.0
1.4	32.0
1.5	38.0
1.6	51.5
1.7	59.0
1.8	68.5
1.9	73.0
1.98	83.0

(vide curve No. 111)

TABLE CXXVII

Conc. of Cr(iii) = 5 m.mole

Conc. of KCl = 0.5 N

Drop time = 3.1 sec.

Sensitivity = 20 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.1	-10.0
0.2	-10.0
0.3	- 9.0
0.4	-8 .0
0.5	- 5.0
0.6	- 2.0
0.7	- 1.5
0.8	- 0.5
0.9	3.5
1.0	11.5
1.1	19.0
1.2	24.0
1.3	26.0
1.4	31.0
1.5	40.0
1.6	56.0
1.7	65.0
1.8	69.0
1.9	74.0
1.98	85.0

(Vide curve No. 112)

T A B L E CXXVIII.

Summary of the results:

Conc. of Cr(iii)	Conc. of KCl	Curve No.	E'/2* (- volt)	E"/2** (-volt)	Remarks
Readings with freshly prepared green chromic chloride solution.					
1.0 m.mole	0.1 N	78	0.78	1.56	The first wave
" "	0.5 N	79	0.79	1.56	is not sharp;
" "	2.0 N	80	0.80	1.56	the reduction
2.5 "	0.1 N	81	0.78	1.57	irreversible.
" "	0.5 N	82	0.78	1.56	The 2nd wave
" "	2.0 N	83	0.80	1.56	is quite sharp
5.0 "	0.1 N	84	0.78	1,56	in every case.
" "	0.5 N	85	0.79	1.56	
" "	2.0 N	86	0.80	1.56	
Readings with aged sample of green chromic chloride solution.					
1.0 m.mole	0.1 N	87	0.95	1.56	
" "	0.5 N	88	0.96	1.56	
" "	2.0 N	89	0.96	1.56	
2.5 "	0.1 N	90	0.94	1.55	Both waves are
" "	0.5 N	91	0.95	1.56	quite sharp.
" "	2.0 N	92	0.96	1.56	
5.0 "	0.1 N	93	0.95	1.57	
" "	0.5 N	94	0.96	1.56	
" "	2.0 N	95	0.96	1.56	
Readings with violet solution of chromic chloride					
1.0 m.mole	0.1 N	96	0.98	1.58	
" "	0.5 N	97	0.99	1.57	
" "	2.0 N	98	1.01	1.57	
2.5 "	0.1 N	99	0.99	1.58	Both waves are
" "	0.5 N	100	1.00	1.58	quite sharp.
" "	2.0 N	101	1.01	1.57	
5.0 "	0.1 N	102	1.00	1.57	
" "	0.5 N	103	1.01	1.58	
" "	2.0 N	104	1.01	1.58	
Readings with Cr(iii) solution obtained by the oxidation of $CrCl_2$					
1.0 m.mole	0.1 N	105	1.08	1.52	
" "	0.5 N	106	1.10	1.56	Waves are quite
" "	2.0 N	107	1.11	1.56	drawn out; a
2.5 "	0.1 N	108	1.10	1.54	small anodic
" "	0.5 N	109	1.12	1.56	wave observed in
" "	2.0 N	110	1.12	1.56	every case.
5.0 "	0.1 N	111	1.11	1,55	
" "	0.5 N	112	1.13	1.56	

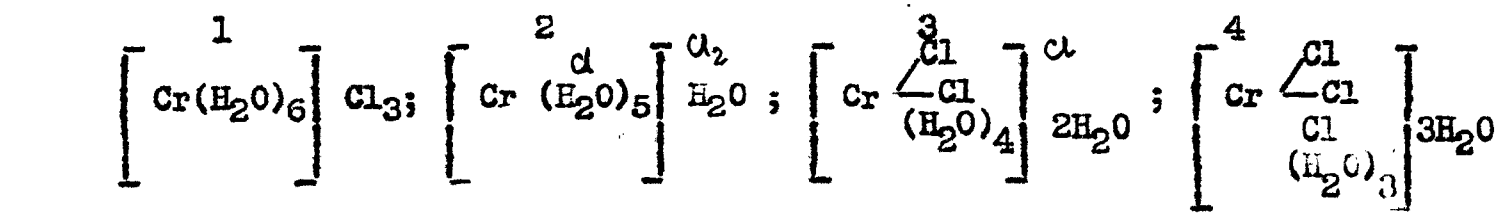
* Half wave potential for the reaction $Cr^{\bullet\bullet\bullet} - e = Cr^{\bullet\bullet}$

** " " " " " " " $Cr^{\bullet\bullet\bullet} - 3e = Cr$

Discussion:

The following observations are made from the reduction of the various varieties of Cr(iii) at the dropping mercury electrode (i) Higher concentrations of the supporting electrolyte KCl make the half wave potential for the first stage reduction Cr(iii) —— Cr(ii), more negative but the second step Cr(iii)——Cr is independent of its concentration. (ii). Freshly prepared solution of the green hydrate has the lowest valu for E/1/2 (-0.8) while the highest value (.1.1 v) is obtained for the oxidised chromous chloride. Also the first stage reduction is very slow in the case of freshly prepared green sample. The half wave potential for the violet sample is higher than that the aged solution of green hydrate (-0.99 and -0.95 respectively). (iii). The waves are quite drawn but in the case of the sample obtained by the oxidation of chromous chloride. This solution, even after exposure for two days and then bubbling air for about half an hour, gave a small anodic wave with E/2 -0.45 Also unlike with all other samples the second wave is also not very shar

The above observations throw much light on the various forms of aquated chromic ions and their stability towards reduction at a dropping mercury electrode. It is evident that the freshly prepared solution of the green hydrate is most easily reducible(E/2 -0.8 v) and that sample obtained by the air oxidation of blue chromous chloride, mos difficulty reducible (E/2-1.11 V). The well known varieties of chromic chloride are



Violet (or greenish blue) | Pale green (Bjerrum's salt) | Green (Werner's salt) | Recourd's chlori

Inference:

(1). Higher concentrations of the supporitng electrolyte KCl make the half wave potential for the first stage reduction more negative.

(2). The half wave potential for the second step is not effected by the concentration of KCl.

(3). The concentration of Cr(iii) does not seem to affect the halfwave potential for either stage.

(4). The E/2 value for the second step is almost the same for all the varieties of Cr(iii).

(5). The height of the second wave is disproportionately large for every sample.

(6). The value of E/2 (for the first step) for the freshly prepared green solution is the lowest and that for the sample obtained by the atmospheric oxidation of chromous chloride, is the highest(-0.785 V. and -1.15 v respectively.

(7). The violet sample has E/2 value higher than that for the aged green sample though the latter also acquires violet colour on aging(the values being -1.00 and -0.955 respectively).

(8). The waves are quite drawn out in the case of the sample obtained by the oxidation of chromous chloride. This sample always gives an anodic wave with E/2 equal to -0.45 volt. The second wave is not very sharp in this case though it is quite sharp in the case of all the other samples.

The solution of the green salt turns slowly to violet on standing. Also the blue chromous chloride solution on air oxidation turns slowly violet which shows that the violet variety is the most stable in solution. The half wave potential of the violet variety was found to be 0·99 which is in agreement with the above. The aged solution of the green hydrate was reduced at a pot. of -0.95, only a little lower value than for the violet sample.

The highest (-ve) value for the oxidation —— reduction potential of the chromic solution obtained from chromous chloride shows that it contains a more stabler complex ion. Since air oxidation is carried out in ' neutral ' medium in the absence of any doner or acceptor ion, it is quite probable that a sort of oxygen bridge is established, like $CrCl_2.-O.CrCl_2$. This complex is quite stable and is very difficultly reducible at the dropping electrode. These conclusions any way, require further experimental support.

STUDIES ON SOME ASPECTS OF THE ANODIC WAVE OF Cr(ii) AND THE COMPOSITE WAVE OF Cr(ii) AND Cr(iii).

In the preceeding paragraphs intresting behaviour regarding the halfwave potentials of chromic ions from different varieties of chromic solutions has been recorded. Similar results were obtained from potentiometric studies where it was found that the steady potential attained by the chromous-chromic system altered disproportionately on adding chromic chloride to the freshly prepared blue chromous chloride solution. With a view to have a clue or insight into this phenomenon, it was thought worthwhile to carryout some studies on the wave characteristics of Cr(ii) and also on the composite waves of mixtures of Cr(ii) and Cr(iii).

Very little seems to have been done on the wave characteristics of chromium (ii). The investigations carried out in this direction are (i) The anodic wave of chromous ions in sulphuric acid for the determination of chromium in steel[9]; (ii) The study of chromo-chromicyanide at the dropping mercury electrode[10]; and (iii) The investigations carried out by Lingane and Pecsock[4] on the anodic waves produced in various supporting electrolytes.

This chapter includes my observations on the polarographic studies on the oxidation of chromous ions in the presence of various salts and complexing agents, and also of chromous solutions oxidised to various degrees by pure hydrogen peroxide solution. The latter was done with a view to achieve conditions whereby chromous solution containing varying amounts of chromic ions could be obtained.

EXPERIMENTAL:

Apparatus: The fischer electropode and electrode assembly described in proceeding pages were used for these experiments.

Reagents: A fresh 'neutral' sample of chromous chloride solution was prepared and transferred to the storage flask. The solution was standardised by the method already described (vide page 12). The readings are given below:

Volume of permanganate taken	= 10.0 c.c.
Strength of permanganate solution	= 0.105 N
Volume of chromous chloride added	= 2.0 c.c.
Strength of ferrous ammonium sulphate(potentiometrically determined)	$= \frac{5 \times 0.105}{5.3}$ = 0.0991 N
Volume of ferrous solution required to reduce the excess permanganate(from titration curve)	= 3.70 c.c.
Volume of ferrous solution equivalent to permanganateused up by chromous chloride	= 6.9 c.c.
Strength of chromous chloride solution	= 0.3418 N

Total chromium in the sample:

Volume of solution used for oxidation	= 1.0 c.c.
Volume of ferrous solution required to reduce the dichromate formed(potentiometrically determined)	= 11.1 c.c.
Concentration of total chromium in moles/litre	= 0.3667

Ratio of Cr(iii)/Cr(ii):

Concentration of Cr(iii) in the sample in moles/litre	= 0.0249
RatioCr(iii)/Cr(ii)	= 0.07286

Since the above solution was too concentrated for the polarographic work, it was diluted in the storage flask itself to a strength of about 0.05 M by pumping in air free distilled water

and neutralised. (The strength was found to be 0.052 N after dilution so that 7.0 c.c. after weighing diluted to 20.00 c.c. in the volumetric flask was 2.6 m.molar solution.)

A solution of 0.01 N hydrogen peroxide was prepared by diluting pure hydrogen peroxide with air free double distilled water and standardising against potassium permanganate solution.

Gelatine was used as maxima suppressor in all these experiments. All the supporting electrolytes were prepared from reagent grade chemicals.

Procedure:

The following method was adopted for carrying out the polarographic measurements.

A calculated volume (say x c.c.) of the supporting electrolyte(to give 0.1 N solution on dilution to 20.0 c.c.) was taken in the cell and 1 c.c. of 0.1 % gelatine added to it. If say, y c.c. was the volume of chromous chloride to be added to give the desired concentration (1 or 2 m.molar), then 20-(x + y + 1) c.c. of double distilled water was added to it and purified nitrogen was bubbled through the mixture. After complete deoxygenation, y c.c. of $CrCl_2$ was added carefully to the cell from the microburette of the storage flask, keeping the current of nitrogen all the time. The polarograms of the chromous-chromic mixture was then recorded. When ever the composition of the chromium solution was to be changed by the addition of Cr(iii) with hydrogen peroxide, then the quantity of water added to make up the total volume also c.c. was 20- (x+y+z+1) c.c. where z stands for the amount of H_2O_2 added.

Hydrogen peroxide which is added can also oxidise the mercury, specially in presence of supporting electrolyte like potassium chloride, but there is very little possibility of this when it is used

in presence of chromous chloride which is a powerful reducing agent.

Polarograms for the residual current were taken with each electrolyte and corrections applied wherever necessary. The second wave for the reduction of Cr(iii) was not recorded as it was not of much significance and above all was not necessary for this work. The readings with the different electrolyte are given below:

Readings with KCl as base electrolyte.

The concentrations of 1.0 M KCl and 0.005 % gelatine were kept constant in all these experiments.

TABLE CXXIX.

Readings for residual current

Sensitivity of the electropode = 5 X

Drop time = 2.9 sec.

A Potential applied (in volts)	Galv. readings (in m.m.)
0.0	-1.0
0.1	-0.5
0.2	-0.25
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.0
0.7	0.0
0.8	0.25
0.9	0.5
1.0	0.5
1.1	0.75
1.2	0.75
1.3	0.9
1.4	1.0
1.5	1.0
1.6	1.0
1.7	1.25
1.8	1.75
1.9	5.5
2.0	36.0

(Vide curve No. 113)

TABLE CXXX

Vol. of H_2O_2 added = 0 c.c.

Conc. of Cr(ii) = 2 m.mole

Conc. of Cr(iii) = 0.146 m.mole

Ratio of Cr(iii)/Cr(ii) = 0.073

Drop time = 2.85 sec.

Sensitivity = 5 X

Potential applied (in volts)	Galv. readings (in m.m.)
0.0	-36.5
0.1	-36.1
0.2	-37.5
0.3	-38.0
0.4	-36.5
0.5	-25.5
0.55	-14.25
0.6	-5.5
0.7	0.0
0.8	0.5
0.9	1.0
1.0	3.75
1.1	7.25
1.2	9.0
1.3	3 9.5
1.4	13.0
1.5	39.0
1.6	84.0

(vide curve No. 114)

TABLE CXXXI

Percentage oxidised by H_2O_2 = 25 %
(1 c.c. - H_2O_2 - 0.77 c.c. $CrCl_2$)

Conc. of Cr(ii) = 1.5 m.mole

Conc. of Cr(iii) = 0.646 m.mole

Ratio of Cr(iii)/Cr(ii) = 0.4305

Drop time = 2.9 sec.

Sensitivity = 5 X

Potential applied (in volts)	Galv. readings (in m.m.)
0.0	-27.2
0.1	-27.0
0.2	-27.5
0.3	-27.0
0.4	-25.5
0.5	-19.75
0.6	-5.0
0.7	0.0
0.8	2.25
0.9	3.5
1.0	6.6
1.1	14.0
1.2	18.0
1.3	19.2
1.4	20.5
1.5	29.5

(Vide curve No, 115)

TABLE CXXXII

Percentage oxidised by H_2O_2 = 50%

Conc, of Cr(ii) = 1 m.mole

Conc. of Cr(iii) = 1.46 m.mole

Ratio Cr(iii)/Cr(ii) = 1.146

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-19.0
0.1	-18.75
0.2	-19.0
0.3	-19.0
0.4	-18.0
0.5	-13.5
0.6	-3.5
0.7	1.5
0.8	4.25
0.9	8.0
1.0	15.0
1.1	13.5
1.2	27.0
1.3	28.25
1.4	31.0
1.5	49.5

(Vide curve No. 116)

TABLE CXXXIII

Percentage oxidised by H_2O_2 = 75%

Conc. of Cr(ii) = 0.5 m.mole

Conc. of Cr(iii) = 1.646 m.mole

Ratio Cr(iii)/Cr(ii) = 3.29

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.).
0.0	-9.75
0.1	-10.0
0.2	-10.0
0.3	-9.5
0.4	-8.5
0.5	-5.25
0.6	0.0
0.7	2.25
0.8	6.0
0.9	13.5
1.0	24.0
1.1	33.0
1.2	36.75
1.3	37.5
1.4	39.0
1.45	53.0

(Vide curve No. 117)

T A B L E CXXXIV

Percentage of Cr(ii) oxidised = 100 %

Concentration of Cr(iii) = 2.146 m.mole.

Drop time = 2.9 sec.

Sensitivity = 5 X

Potential applied (in volts)	Galv. readings (in m.m.)
0.0	-2.0
0.1	-1.5
0.2	-1.2
0.3	-0.5
0.4	0.6
0.5	0.0
0.6	0.0
0.7	3.0
0.8	9.25
0.9	19.0
1.0	30.0
1.1	40.5
1.2	45.0
1.3	46.2
1.4	47.75
1.45	60.0

(Vide curve No 118)

Summary of the readings with KCl (1 N).

TABLE CXXXV.

Curve No.	Conc. of Cr(ii)	Conc. of Cr(iii)	Ratio Cr(ii)/Cr(iii)	A E/2	C E/2	Remarks
114	2 m.molo	0.143 m.molo	0.073	-0.53	-1.09	The potential for the two waves remains almost the same reduction is possible.
115	1.5 "	0.643 "	0.431	-0.52	-1.08	
116	1.0 "	1.143 "	1.143	-0.52	-1.05	
117	0.5 "	1.643 "	3.29	-0.52	-1.0	
118	0.0 "	2.143 "	-	-	-0.98	

Readings with potassium sulphate (1 N).

The above experiments, under identical conditions were also repeated with 1 N solution of potassium sulphate as supporting electrolyte. The readings are tabulated as follows:-

TABLE CXXXVI.

Readings for residual current.

Potential applied (in volts)	Galv. readings (in m.m.)
0.0	0
0.1	0
0.3	0
0.5	0.5
0.7	0.5
0.9	0.75
1.1	0.75
1.3	0.75
1.5	1.0
1.8	2.0
1.85	3.0
1.95	41.75

(Vide curve No. 119)

TABLE CXXXVII.

Percentage oxidised by H_2O_2 = 0.0

Conc. of Cr(ii) = 2 m.mols

Conc. of Cr(iii) = 0.146

Ratio Cr(iii)/Cr(ii) = 0.073

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	+35.5
0.1	+30.6
0.2	+25.0
0.3	+20.75
0.4	+4.25
0.5	0.0
0.6	0.0
0.71	0.25
0.8	0.25
0.9	0.25
1.0	0.5
1.1	2.75
1.21	5.5
1.3	7.0
1.4	17.5
1.45	52.0

(Vide curve No. 120.)

TABLE CXXXVIII.

Percentage oxidised = 25 %

Conc. of Cr(ii) = 1.5 m.mols

Conc. of Cr(iii) = 0.646

Ratio Cr(iii) Cr(ii) = 0.4305

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.).
0.0	+22.0
0.11	+27.5
0.2	+25.75
0.3	+13.0
0.4	+3.0
0.51	0.0
0.6	0.5
0.7	0.6
0.8	1.5
0.9	2.0
1.01	4.0
1.1	10.5
1.2	13.0
1.31	15.0
1.4	25.0
1.45	51.0

(Vide curve No. 121.)

TABLE CXXXIX.

Percentage oxidised	= 50 %
Conc. of Cr(ii)	= 1.m.mole
Conc. of Cr(iii)	= 1.146
Ratio Cr(iii)/Cr(ii)	= 1.146
Drop time	= 2.9 sec.
Sensitivity	= 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-18.0
0.1	-18.0
0.2	-17.0
0.3	-10.25
0.4	- 1.5
0.5	- 1.0
0.6	3.0
0.7	3.75
0.8	5.0
0.9	6.5
1.0	12.0
1.1	20.0
1.2	21.75
1.3	23.5
1.4	40.6

(Vide curve No. 122.)

TABLE CXL.

Percentage oxidised	= 75 %
Conc. of Cr(ii)	= 0.5 m.mole
Conc. of Cr(iii)	= 1.646
Ratio Cr(iii)/Cr(ii).	= 3.29
Drop time	= 2.85 sec.
Sensitivity	= 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-9.25
0.1	-9.0
0.2	-9.0
0.3	-6.5
0.4	-1.5
0.5	2.0
0.6	5.0
0.7	7.5
0.8	11.0
0.9	17.5
1.0	26.0
1.1	35.0
1.2	36.75
1.3	40.0
1.4	40.0

(Vide curve No. 123.)

T A B L E CXLI

Percentage oxidised	= 100%
Conc. of Cr(ii)	= 0.0
Conc. of Cr(iii)	= 2.146 m.mole
Drop time	= 2.9 sec.
Sensitivity of apparatus	= 5 X

Potential applied (in volts)	Galv. readings (in m.m.).
0.0	-0.5
0.1	-0.25
0.2	-0.25
0.3	0.0
0.4	0.5
0.5	2.0
0.6	5.0
0.7	7.5
0.8	11.0
0.9	17.75
1.0	23.0
1.1	34.5
1.2	37.0
1.3	39.5
1.4	51.0
1.45	67.0

(Vide curve No. 124.).

Summary of the readings with K_2SO_4(1 M).

Curve No.	Conc. of Cr(ii)	Conc. of Cr(iii).	Ratio of Cr(ii)/Cr(iii)	A E/2	C E/2	Remarks
120	2 m.mole	0.146 m.mole	0.073	- .32	-1.0	E/2 values
121	1.5 m.mole	0.646 m.mole	0.431	- .30	-1.06	almost const.
122	1.0 m.mole	0.646 m.mole	0.431	- .31	-1.03	Reduction
123	0.5 m.mole	0.646 m.mole	3.29	- .32	-0.98	irreversible.
124	0.0 m.mole	2.146 m.mole	-	-	-0.93	

Readings with in presence of HCl (1 M).

TABLE CXLII.

Readings for residual current.

Drop time = 2.9 sec.

Sensitivity of apparatus = 5 X

Pot. applied (in volts)	galv. readings (in m.m.)
0.0	-0.5
0.1	-0.25
0.2	0.0
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.0
0.7	0.0
0.8	0.25
0.9	0.5
1.0	0.5
1.1.	0.75
1.2	1.0
1.3	1.5
1.4	2.25
1.5	10.25
1.6	64.0

(Vide curve No. 125)

TABLE CXLIII.

Percentage oxidised = 0.0

Conc. of Cr(ii) = 2 m.mole

Conc. of Cr(iii) = 0.145

Drop time = 2.9 sec.

Sensitivity of apparatus = 5 X

Pot. applied (in volts)	galv. readings (in m.m.)
0.0	-35.75
0.1	-35.25
0.2	-36.5
0.3	-37.0
0.4	-36.5
0.5	-35.5
0.6	-30.0
0.7	-3.0
0.8	0.0
0.9	0.0
1.0	0.5
1.1	3.5
1.2	3.75
1.3	5.25
1.4	10.0
1.5	23.0

(Vide curve No. 126)

TABLE CXLIV.

Percentage of Cr(ii)oxidised = 25%

Conc. of Cr(ii) = 1.5 m.mole

Conc. of Cr(iii) = 0.646

Ratio Cr(iii)/Cr(ii) = 0.431

Drop time = 2.95 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-23.75
0.1	-27.0
0.2	-27.0
0.3	-26.5
0.4	-25.5
0.5	-24.0
0.6	-13.0
0.7	-2.5
0.8	0.0
0.9	[illegible]
1.0	[illegible]
1.1	11.0
1.2	[illegible]
1.3	[illegible]
[illegible]	20.0
1.45	32.5

(Vide curve No. 127)

TABLE CXLV.

Percentage of Cr(ii)oxidised = 50 %

Conc. of Cr(ii) = 1.m.mole

Conc. of Cr(iii) = 1.146

Ratio Cr(iii)/Cr(ii) = 1.146

Drop time = 2.9 sec.

Sensitivity = 5 A

Pot. applied ([illegible])	Galv. readings (in m.m.)
0.0	-18.5
0.1	-18.0
0.2	-18.0
0.3	-17.5
0.4	-16.0
0.5	-15.0
[illegible]	-9.0
[illegible]	-1.5
[illegible]	-0.5
0.9	1.0
1.0	7.0
[illegible]	17.0
1.2	21.0
[illegible]	22.5
1.4	[illegible]
1.45	[illegible]

(Vide curve No. 128)

TABLE CXLVI.

Percentage of Cr(ii) oxidised = 75%

Conc. of Cr(ii) = 0.5 m.mole

Conc. of Cr(iii) = 1.646 m.mole

Ratio Cr(iii)/Cr(ii) = 3.29

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-9.5
0.1	-9.75
0.2	-9.5
0.3	-9.0
0.4	-9.0
0.5	-8.25
0.6	-6.0
0.7	-2.0
0.8	1.0
0.9	4.0
1.0	7.5
1.1.	15.0
1.2	30.25
1.3	32.0
1.4	39.5

(Vide curve No. 129)

TABLE CXLVII.

Percentage oxidised = 100%

Conc. of Cr(ii) = 0.0

Conc. of Cr(iii) = 2.146

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-1.0
0.1	-0.5
0.2	-0.25
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.0
0.7	0.25
0.8	1.5
0.9	6.5
1.0	17.0
1.1	32.0
1.2	38.5
1.3	41.5
1.4	46.5
1.45	58.0

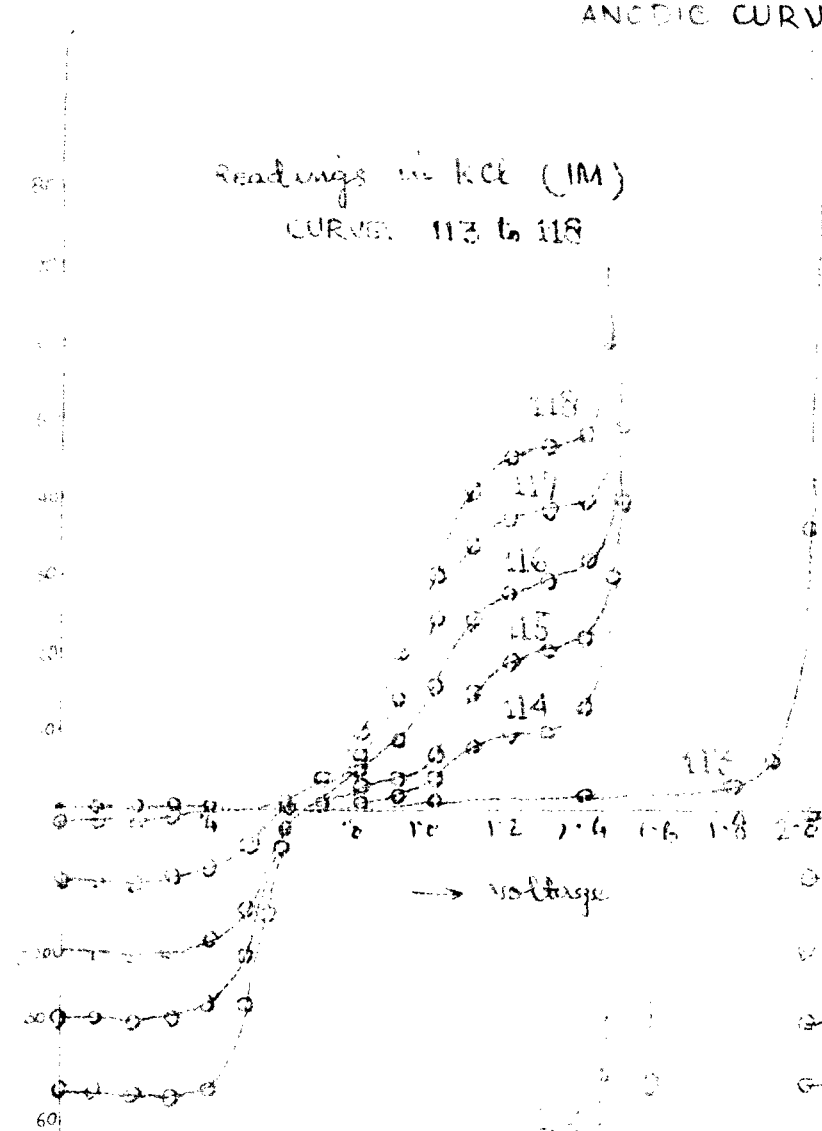
(Vide curve No. 130)

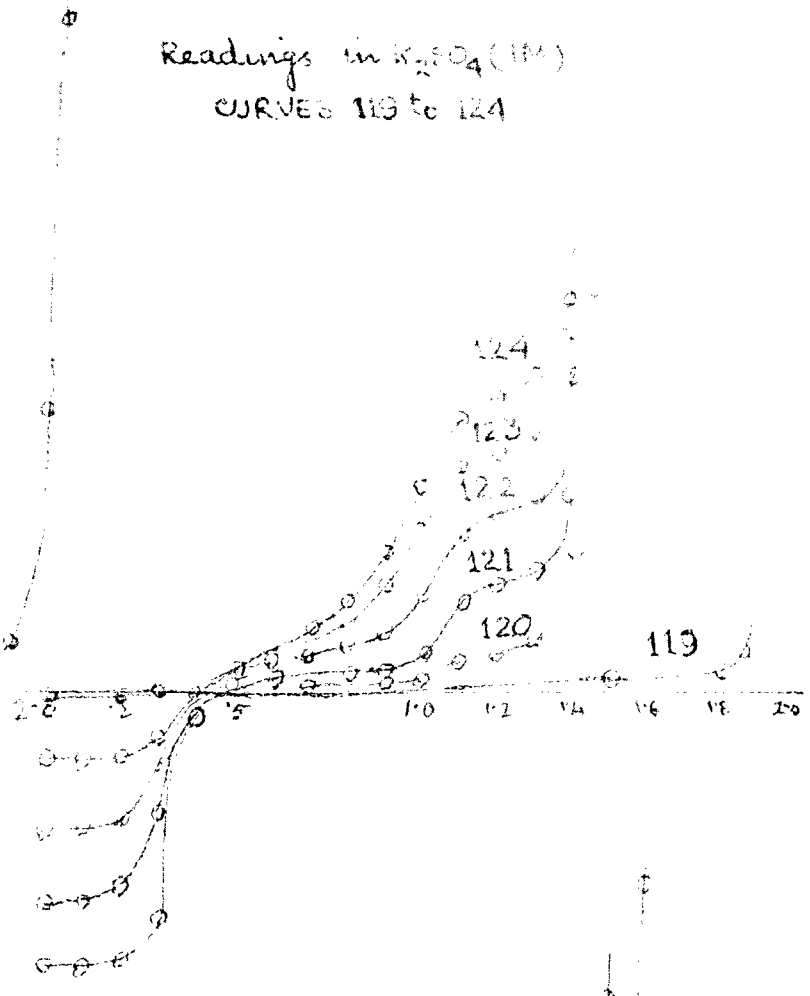
Summary of the readings in HCl (1 M).

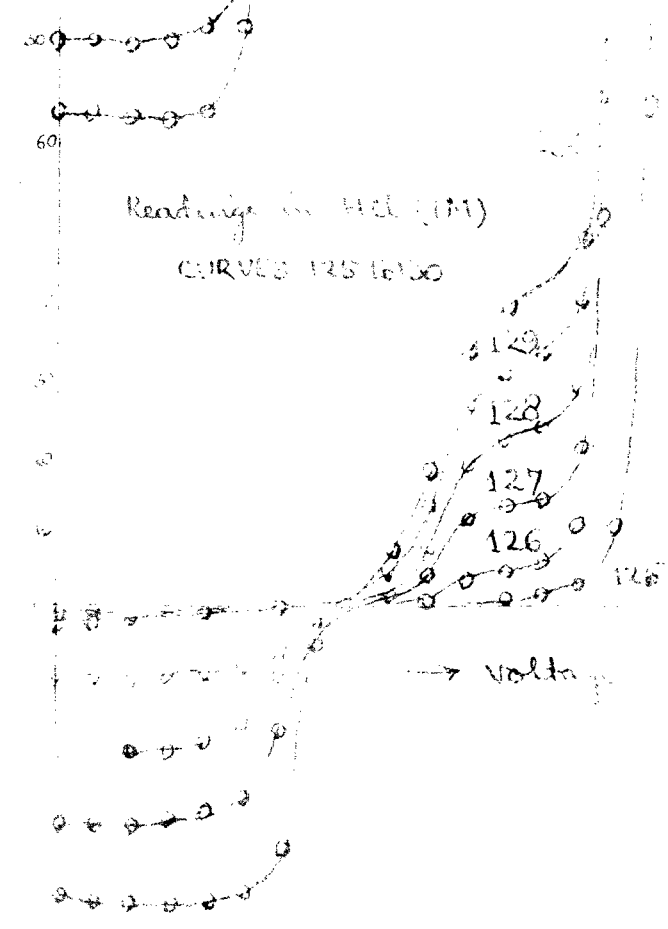
T A B L E CXLVIII

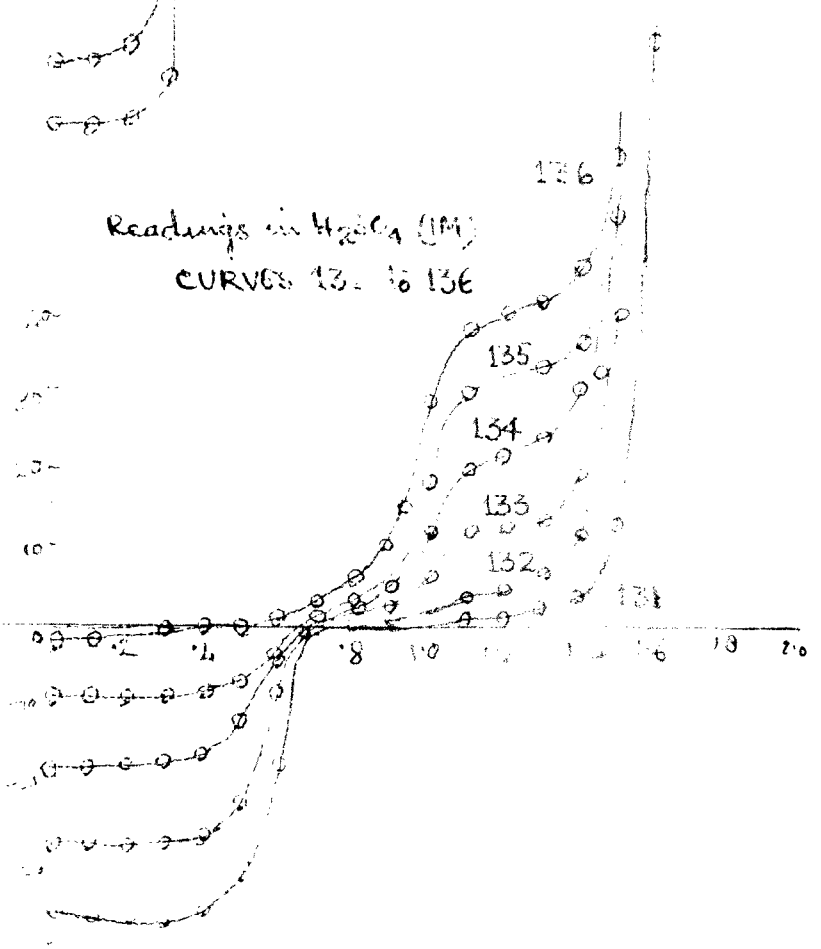
Curve No.	Conc. of Cr(ii)	Conc. of Cr(iii)	Ratio Cr(ii)/Cr(iii)	A E/2	C E/2	Remarks
126	2 m.mole	o.146	0.073	- .64	1.06	
127	1.5 m.mole	o.646	0.431	- .62	1.04	
128	1.0 m.mole	1.146	1.146	- .62	1.04	Reduction irreversible
129	0.5 m.mole	1.646	3.29	- .64	1.06	
130	0.0	2.146	-	-	1.08	

ANODIC CURVES OF Cu(II)









Readings in presence of H_2SO_4 (1 M).

Readings for residual current.

TABLE CXLIX.

Drop time = 2.9 sec.

Sensibivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-0.5
0.1	-0.25
0.2	-0.25
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.0
0.7	0.25
0.8	0.25
0.9	0.5
1.0	0.5
1.1	1.0
1.2	1.25
1.3	2.0
1.4	3.75
1.5	13.0
1.6	74.5

(Vide curve No. 131)

TABLE CL.

Percentage oxidised = 0.0

Conc. of Cr(ii) = 2 m.mole

Conc. of Cr(iii) = 0.146

Ratio Cr(ii)/Cr(iii) = 0.073

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (invlts)	Galv. readings (in m.m.)
0.0	-37.0
0.1	-37.25
0.2	-37.0
0.3	-37.0
0.4	-36.5
0.5	-31.25
0.6	-17.5
0.7	-0. 25
0.8	0.0
0.9	0.25
1.0	2.0
1.1	3.25
1.2	4.0
1.3	6.0
1.4	11.25
1.5	39.5

(Vide curve No. 132)

TABLE CLI.

Percentage oxidised = 25%

Conc. of Cr(ii) = 1 m.mole

Conc. of Cr(iii) = 0.646

Ratio Cr(ii)/Cr(iii) = 0.431

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-28.0
0.1	-27.5
0.2	-28.0
0.3	-28.25
0.4	-27.75
0.5	-22.5
0.6	0.15
0.7	0.25
0.8	1.0
0.9	2.25
1.0	6.0
1.1	11.5
1.2	12.25
1.3	13.5
1.4	19.0
1.45	32.5

(Vide curve No.133)

TABLE CLII.

Percentage oxidised =50%

Conc. of Cr(ii) = 1 m.mole

Conc. of Cr(iii) = 1.146

Ratio Cr(iii)/Cr(ii) = 1.146

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-18.5
0.1	-18.25
0.2	-18.0
0.3	-17.5
0.4	-17.0
0.5	-12.6
0.6	-4.25
0.7	0.0
0.8	1.5
0.9	4.75
1.0	12.0
1.1	20.0
1.2	21.5
1.3	23.25
1.4	30.0
1.5	52.5

(Vide curve No. 134)

TABLE CLIII

Percentage oxidised = 75%

Conc. of Cr(ii) = 0.5 m.mole

Conc. of Cr(iii) = 1.646

Ratio Cr(ii)/Cr(iii) = 3.29

Drop time = 2.9 sec

Sensitivity = 5X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-9.75
0.1	-9.25
0.2	-9.0
0.3	-9.0
0.4	-8.75
0.5	-7.5
0.6	-2.5
0.7	0.5
0.8	5.25
0.9	5.5
1.0	18.0
1.1	29.5
1.2	32.0
1.3	33.0
1.4	36.0
1.45	46.5

(Vide curve No. 135)

TABLE CLIV

Percentage oxidised = 100%

Conc. of Cr(ii) = 0.0

Conc. of Cr(iii) = 2.146 m.mole

Ratio Cr(ii)/Cr(iii) = —

Drop time = 2.9 sec.

Sensitivity = 5 X

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-1.5
0.1	-1.0
0.2	-0.5
0.3	0.0
0.4	0.0
0.5	0.0
0.6	0.5
0.7	3.0
0.8	5.5
0.9	10.75
1.0	28.5
1.1	38.0
1.2	40.0
1.3	41.25
1.4	46.0
1.5	60.0

(Vide curve No. 136)

Summary of the readings in H_2SO_4(1 M)

TABLE CLV.

Curve No.	Conc. of Cr(ii)	Conc. of Cr(iii)	Ratio Cr(iii)/Cr(ii)	A E/2	C E/2	Remarks
132	2.0 m.mole	0.146	0.073	0.58	1.0	
133	1.5 m.mole	0.646	0.431	0.56	1.02	Reduction
134	1.0 m.mole	1.146	1.146	0.54	1.02	irreversible
135	0.5 m.mole	1.646	3.29	0.55	0.98	
136	0.0 m.mole	2.146	-	-	0.98	

From the above sets of readings (with KCl, K_2SO_4, HCl and H_2SO_4) no shift either in the anodic or the cathodic halfwave potential is observed by changing the composition.of the solution (i.e. the chromic-chromous ratio by the oxidation with H_2O_2) For the rest of the experiments on anodic wave, therefore, only one reading for each set was taken. A solution containing about equal quantities of chromous and chromic ions was thought preferable since the characteristic of both the cathodic and anodic waves could be studied at the same time. For this, as in the previous cases, the chromous solution was transferred to the polarographic cell and 50 % of it oxidised by the addition of the calculated amount of hydrogen peroxide and the polarograms taken. Readings were also taken with mixtures of KCl-HCl, K_2SO_4- H_2SO_4 and HAc-NaAc The following experimental conditions were maintained in all the experiments.

(i). Percentage of Cr(ii) oxidised = 50 %
(ii). Concentration of Cr(ii) = 1 m.mole.
(iii). Concentration of Cr(iii) = 1.146 m.mole.
(iv). Ratio Cr(iii)/Cr(ii) = 1.146.
(v). Sensitivity of the apparatus = 5 X.

Readings with KCl(0.5 N)+HCl(0.5 N)

50%

TABLE CLVI

Drop time = 2.85 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-19.0
0.1	-19.25
0.2	-19.5
0.3	-19.0
0.4	-18.5
0.5	-17.0
0.6	-12.25
0.7	1.5
0.8	0.0
0.9	0.5
1.0	5.0
1.1	17.5
1.2	21.0
1.3	21.75
1.4	24.25
1.5	[illegible]

(Vide curve No. 137)

$E_{\frac{1}{2}} - E_{\frac{1}{3}}$ = 0.09; -0.09

Anodic potential = 0.30

Cathodic potential = -1.04

Readings with H_2SO_4, K_2SO_4 (0.5 each)

50 %

TABLE CLVII

Drop time = 2.9 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-17.0
0.1	-17.25
0.2	-16.75
0.3	-16.0
0.4	-11.0
0.5	-2.5
0.6	0.0
0.7	0.0
0.8	0.0
0.9	0.5
1.0	8.0
1.1	17.75
1.2	20.0
1.3	21.5
1.4	24.0
1.5	25.5

(Vide curve No. 138)

$E_{\frac{1}{2}} - E_{\frac{1}{3}}$ = 0.08; -0.1

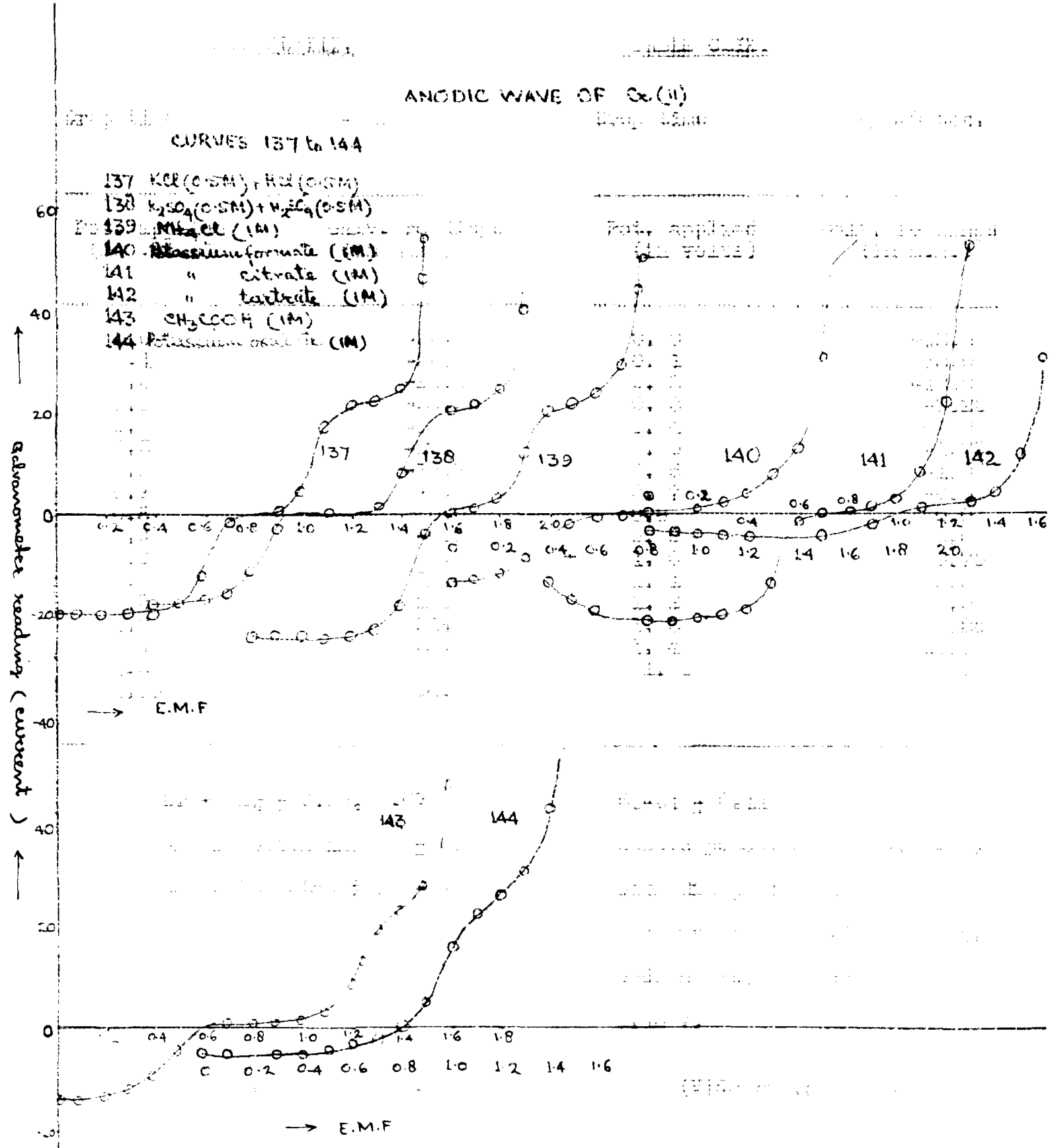
Anodic potential = (-0.4)

Cathodic potential = -1.02

ANODIC WAVE OF Co.(II)

CURVES 137 to 144

137 KCl (0·5M) + HCl (0·5M)
138 K_2SO_4 (0·5M) + H_2SO_4 (0·5M)
139 NH_4Cl (1M)
140 Potassium formate (1M)
141 " citrate (1M)
142 " tartrate (1M)
143 CH_3COOH (1M)
144 Potassium oxalate (1M)



Readings with NH_4Cl (1 N).

TABLE CLVIII.

Drop time = 2.95 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-23.5
0.1	-24.0
0.2	-24.0
0.3	-24.25
0.4	-23.5
0.5	-22.5
0.6	-17.75
0.7	-4.0
0.8	0.0
0.9	-0.5
1.0	3.0
1.1	11.5
1.2	20.0
1.3	21.25
1.4	23.0
1.5	29.0
1.55	44.0

$E_{\frac{1}{2}}^{a} - E_{\frac{1}{2}}^{c}$ = 0.09, 0.07

Anodic potential = 0.65

Cathodic potential = -1.5

(Vide curve No. 139)

Readings with potassium ferrocyanide.

TABLE CLIX.

Drop time = 2.9 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-13.5
0.1	-13.0
0.2	-12.0
0.3	-3.25
0.4	-4.0
0.5	-1.75
0.6	-1.0
0.7	-0.5
0.8	0.0
0.9	0.0
1.0	0.75
1.1	2.0
1.2	4.0
1.3	7.25
1.4	12.5
1.5	20.0

$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ = 0.11

Anodic potential = (-0.22)

Cathodic potential =

The wave is not well defined.

Diffusion current is constant at

1.45 V.

(Vide curve No. 140)

TABLE CLX.

READINGS WITH POT. CITRATE.

Drop time = 2.9 sec.

Pot. applied (in volts)	galv. readings (inm.m.)
0.0	-13.0
0.1	-17.0
0.2	-17.25
0.3	-20.5
0.4	-21.0
0.5	-21.0
0.6	-21.0
0.7	-20.0
0.8	-19.0
0.9	-14.25
1.0	-2.0
1.1	0.0
1.2	0.25
1.3	0.5
1.4	2.5
1.5	8.0
1.6	21.5

Anodic potential -

Cathodic potential -

Neither oxidation of Cr(ii) nor reduction of Cr(iii) Sudden increase in current at - 0.95 volts.

(Vide curve No. 141)

TABLE CLXI.

READINGS WITH POT. TARTARATE.

Drop time = 2.9 sec.

Pot. applied (in volts)	galv. readings (in m.m.)
0.0	-3.0
0.1	-4.0
0.2	-4.5
0.3	-4.5
0.4	-5.0
0.5	-5.0
0.6	-5.0
0.7	-4.5
0.8	-4.0
0.9	-3.5
1.0	0.0
1.1	0.5
1.2	1.25
1.3	2.0
1.4	4.0
1.5	11.25
1.6	30.5

Anodic potential -

Cathodic potential -

Neither anodic nor cathodic wave.

(Vide curve No. 142)

Readings with acetic acid (1 M).

TABLE CLXII.

Drop time = 2.9 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-13.5
0.1	-13.25
0.2	-13.0
0.3	-11.0
0.4	-9.5
0.5	-4.25
0.6	0.0
0.7	0.5
0.8	1.0
0.9	1.0
1.0	1.25
1.1	3.0
1.2	9.0
1.3	18.5
1.4	22.0
1.5	27.0
1.6	47.5

$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ = 0.1 , -0.02

Anodic potential $\frac{3}{4}$ (-0.4)

Cathodic potential = (-1.2)

The waves are not well defined

(Vide curve No. 143)

Readings with Pot oxalate (1M).

TABLE CXLIII.

Drop time = 2.95 sec.

Pot. applied (in volts)	Galv. readings (in m.m.)
0.0	-4.5
0.1	-5.0
0.2	-5.0
0.3	-5.0
0.4	-11.75
0.5	-11.5
0.6	-3.5
0.7	-1.5
0.8	0.0
0.9	4.5
1.0	15.0
1.1	21.5
1.2	22.75
1.3	30.4
1.4	42.0
1.5	42.0

$E_{\frac{3}{4}}-E_{\frac{1}{4}}$ = — , -0.10.

Anodic potential

Cathodic potential $\frac{1}{2}$(-0.95)

Cr(ii) does not give an anodic wave in oxalate medium, but Cr(iii) gives a cathodic wave.

(Vide curve No. 144)

The reversibility of the oxidation and reduction processes were also seen by measuring the two values of $E_{\frac{3}{4}}$ and $E_{\frac{1}{4}}$[12] which represents the potentials at which the current is equal to one fourth and three fourth respectively. The values of $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ for a reversible cathodic wave is equal to -0.0564 volts and for a reversible anodic wave is equal to o.o564 volts. Any appreciable deviation from these values was taken as a sign of irreversibility.

The diffusion current constant was also determined in every case. m was determined by collecting the mercury flowing for 15 minutes and found out its weight accurately.[13] The results are summarised as below:

TABLE CLXIV.

Supporting electrolyte.	E/2 for anodic wave.	E/2 for cathodic wave.	id / $C\sqrt{h}$	Curve No.	Remarks.
KCl (1 N)	-0.03	-1.03	-1.04	114-118	Irreversible.
[illegible]	-0.01	-1.02	-1.05	120-124	"
HCl (1 N)	-0.63	-1.05	-1.08	125-130	"
H_2SO_4 (1 N)	-0.55	-1.00	-1.45	132-136	"
KCl (0.5 N), HCl (0.5 N)	-0.60	-1.04	-1.3	137	"
K_2SO_4 (0.5 N) H_2SO_4 (0.5 N)	[illegible]	-1.02	-1.55	138	"
[illegible] (1 N)	-0.65	-1.1	-1.25	139	"
Pot. formate 1 N	0.32	"	1.34	140	Ill defined.
Pot. Citrate 1 N	"	"	"	141	Ill defined. No reduction or oxidation.
Pot. [illegible]ate 1 N	"	"	"	142	"
Acetic acid 1 N	-0.4	(-1.8)	-0.35	143	Ill defined
Pot. [illegible]ate 1 N		(-0.35)	"	144	Ill defined Reoxidation.

Discussion:

The following inferences are drawn from a study of the anodic waves of Cr(ii) in various supprting electrolytes:

(i). The anodic waves of Cr(ii) and the cathodic waves of Cr(iii) show irreversibility wherever, the electrode reaction takes place.

(ii). Chromous ions are oxidised in presence of supporting electrolytes such as titrate and oxalate, (and acetate?). With cirtrate the polarogram is a typical nature, the current decreases first with increasing potential, remains constant for a certain range and suddenly rises at about 0.95 volts.

(iii). The cathodic half wave potential for the reaction Cr(iii) +) $\rightleftharpoons$ Cr(ii) is almost the same in every case and is just above -1.0 volt. Low values are obtained for the anodic E/2 with K_2SO_4 H_2SO_4 , HAc etc.

(iv). Well defined but irreversible waves are obtained with HCl, NH_4Cl, KCl, HCl and H_2SO_4.

While the cathodic E/2 values are not changed very much and remain almost constant, the anodic potentials vary with the supporting electrolyte used. A perusal column No.2 of Table No. 64 shows that E/2 has got the lowest value (negative) in presence of potassium sulphate and highest with HCl , H_2SO_4 and KCl standing next in oder. It is evident that the presence of hydrogen or chloride ions or both are essential for the better utility of chromous chloride as a reducing agent, as seen by the high negative values (anodic E/2) obtained in their presence.

In presence of ammonium chloride E/2 is found to be still higher (-0.65) than with HCl. It appears that ammonium ions have got greater influence than hydrigen ions in determining the role of chromous ions in oxidation reduction reactions.

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CHAPTER V.

STABILISATION OF Cr(ii) BY PREPARING AN INSOLUBLE COMPLEX— STUDY OF ITS PROPERTIES AND COMPOSITION.

One of the methods employed for stabilising highly unstable ions is to prepare complex compounds which are either insoluble or slightly soluble in water. Reference to this fact has already been made in the ' General Introduction '. Chromous ion forms a few complexes with ammonia and dipyridyl but even they are unstable. Potassium ferrocyanide was therefore used as a complexing reagent, and the yellowish green precipitate thus obtained was thoroughly investigated both in the dried and the wet states.

The studies constitute:

1. Composition of the complex by —
   - (a) Chemical analysis.
   - (b) Conductometry.
   - (c) Potentiometry.
   - (d) Amperometric Titrations.
2. Adsorptive and hydrolytic properties of the freshly precipitated complex.

INTRODUCTION.

Investigations on the nature and composition of ferrocyanogen complexes of metal salts present a number of intresting features. It attracted the attention of a number of workers since the later half of the last century, although their work remained

more or less of an empirical nature for more than 50 years. It was only from 1933 onwards that a systematic study of the problem was taken up.

A number of metal complexes of hexacyano ferrite and ferrate are known. These compounds do not exist as complex ions in solution (with the exception of alkali ferrocyanides) and generally form precipitates with low solubility products. They are also characterised by their bright colour of different shades, depending on the excess of either of the reactents. These compounds are also associated with properties like, the tendency to pass over to the colloidal state, their adsorptive and hydrolytic properties and in some cases their tendency to assume a gelatinous character. The determination of the composition of these complex ferrocyanides had been one of the difficult problems facing the workers in the field of study. They were confronted with a number of difficulties due to the intresting behaviour of these precipitates of changing their composition in passing from a freshly precipitated to a dried state. Methods of chemical analysis, therefore, gave erroneous results and conflicting data were available for one and the same compound. Later on physical methods were adopted for elucidating their composition, but these too, specially the potentiometric and thermometric methods, suffer from a number of limitations. Before introducing certain aspects of the study of the complex ferrocyanide undertaken by me, it is worth while to give a brief review of the existing literature.

Extensive work was carried out on metallic ferrocyanides by E.H. Miller[1] and Albert[2] who studied the composition of the

precipitates obtained by the inter-action of potassium ferrocyanide and zinc, manganese and cadmium salts. G.C.Stone and Van Inger[3] found that the composition of the precipitate with manganese salts varied with the medium of precipitation. In neutral medium the composition corresponded to $K_2MnFe(CN)_6$ irrespective of any excess of the reactents; but when the precipitation was carried out in the cold from a solution containing 5 % of HCl by volume, the composition changed to $K_2Mn_4(FeCy_6)_3$. Dicke observed that the use of excess of reagents has great influence on the composition of the precipitates, the proportion of manganese decreasing with increasin g amount of K_4FeCy_6 added and vice versa. I

Intresting observations were made on the change of composition of zinc ferrocyanide by Miller and Danzier.[4] They found that the ratio of iron and zinc varied from 1:1.35 to 1:1.59 under different conditions of precipitation, ageing of the precipitate in the reaction mixture, increasing the proportion of zinc. From a study of the composition of the complex precipitated in acid and ammonical media, they came to the conclusion that it was impossible to obtaine pure $K_2ZnFeCy_6$. Miller and Falk obtained zinc ferrocyanide by adding K_4FeCy_6 to zinc chloride containg ammonium chloride at 60^o and found the compsoition as $Zn(NH_4)K_2FeCy_6Cl$. But, by agitation with KCl at 70^o this gave a simple mixture of $Zn_2FeCy_6$and $K_2ZnFeCy_6$.

The ferrocyanides of nickel and cobalt were studied by Wyrubow[5]and he found that no compound of definite composition was formed . The composition varied differently as $K_2NiFeCy_6$;$K_2Ni_3(FeCy)_6$ Co_2FeCy_6; $K_2Co_7(FeCy_6)_4$; $K_6Co_5(FeCy_6)_4$ etc. G.A. Barbieri[6] obtained a complex of the formula NH_4FeCy_6. 2 $MoO_3$by adding potassium ferro-

cyanide to acidified ammonium molybdate and washing the precipitate with ammonium nitrate and acetate.

Due to these conflicting views of varioues workers on the composition of the complex ferrocyanides, obtained mainly by purely chemical, physico-chemical studies were attempted. Zinc ferrocyanide was studied first by potentiometric estimation of Zinc by K_4FeCy_6. Kolthoff and Verziji found the composition to be $K_2Zn_3(FeCy_6)_2$ and was supported by Mondaine Monval and Paris on the basis of their thermometric titrations.

Gaur and Bhattacharya studied the ferrocyanides of copper cadmium and uranium came to the conclusion that mere analytical study of these complexes could not lead to the establishment of some definite compesition and also due to their tendency to pass into the colloidal state. This was in agreement with the earlier views of Malik and Bhattacharya[10] on the properties of Prussina and Turnbull's blues.

More recently studies on nickel and cobalt ferrocyanides have been made by Moritz Kohn" and found that Ni_2FeCy_6 is oxidised to to ferrocyanide by atmospheric oxygen. Co_2FeCy_6 is also oxidised under the same conditions. They also proved that some of the statements of former investigators on reactions of Ni and Co salts with potassium ferrocyanide and ferricyanide are erroneous and some of their iron cyanogen compounds described in literature do not exist at all.

An empirocal study of the solubilities of ferrocyanides has been made by R.V.Vorn-ste-we[12] . The study was made by the action of K_4FeCy_6 in a neutral or weakly acid(HCl or H_2SO_4) medium in presence of great excess of the precipitant in the solid phase. The relative position of a cation in the series was determined by

its solubility to displace another cation from its ferrocyanide precipitate. Determinations were made in hot and cold media. After the equilibrium was established, the solid and liquid phases were analysed and found its as $Pb^{++} > Al^{+++} > Bi^{++} > Sb^{++} > Mn^{++} > Cd^{++} > Co^{++} > Ni^{++} > Fe^{++} > Zn^{++} > Fe^{+++} > Cu^{++} > Ag^{+}$.

Interestingly enough from the existing literature it is seen that nothing has been done so far to investigate the products obtained by the interaction of potassium ferrocyanide with chromous and chromic salts. It looks very intresting that while chromium in the trivalent state does not react under ordinary conditions, in the divalent state it gives a precipitate by mixing with potassium ferrocyanide(It was taken that Cr(iii) does not react with potassium ferro or ferricyanide but it has been found recently in our laboratories that it does so specially with higher concentrations and at higher temperatures, to give a solid complex ferrocyanide. The composition and nature of this complex is also under investigation). This part of the thesis deals with the study of the composition and properties of the Cr(ii) complex by applying a number of physico-chemical techniques.

(c). Chemical analysis of the [illegible] precipitate.

1. Chromous ferrocyanide :- Preparation:-

The chromous ferrocyanide complex was prepared by mixing chromous chloride and potassium ferrocyanide in different proportions. The reaction takes place at ordinary temperature on mixing the reagent giving at first a gel type precipitate which breaks down on shaking, the colour of the precipitate varies

slightly with the proportion of the reagent and the water content.

(a). Chromous chloride

A"neutral" sample of chromous chloride solution was prepared as described earlier. It was transferred to the storage flask and standardised against potassium permanganate by the back estimation method (vide chapter I page 19) The total chromium in the solution was also estimated.

1. Volume of potassium permanganate used = 10.0 c.c.

2. Strength of permanganate solution (determined against 0.1 N oxalic acid) = 0.102 N

3. Volume of chromous chloride added = 2.0 c.c.

4. Strength of ferrous ammonium sulphate = $\frac{5 \times 0.102}{5.21}$

(formed by potentiometric titration against potassium permanganate) = 0.098 N

5. Volume of ferrous solution required to neutralise excess permanganate (from potentiometric titration curve) = 3.45 c.c.

6. Volume of Fe^{++} solution equivalent to $KMnO_4$ used up by chromous chloride. = 6.97 c.c.

Strength of chromous chloride solution = $\frac{6.97 \times 0.098}{2}$

= 0.3418 N

Total chromium

Volume of chromous solution used for oxidation = 1.0 c.c.

Volume of ferrous solution required to neutralise the dichromate formed (determined potentiometrically = 11.20 c.c.

Concentration of total chromium (in gm. mol. /litre). = $\frac{11.2 \times 0.098}{1 \times 3}$

= 0.366 M

(b). Potassium ferrocyanide.

Potassium ferrocyanide [illegible] strength N/5 is prepared by dissolving 42.3 g. [illegible] (recrystallised) of the reagent grade sample in 500 c.c. of water. The strength of solution was checked up by titrating against standard potassium permanganate.

Proportion of reagents.

To find out the exact proportion of the reagents to give a 'neutral' sample of the complex, the following procedure was adopted.

1.0 c.c. each of potassium ferrocyanide was taken in ten test tubes diluted to about 5 c.c. and covered with a layer of light petrol. Varying quantities of chromous chloride solution were then added to each using the Macalister attachment of the storage flask. The reagents were thoroughly mixed and then centrifuged after five minutes. The supernatant solution was then tested for chromium and ferrocyanide ion. By this method it was then possible to find the proportion of the reagents for the formation of the 'neutral' complex (the supernatant solution giving neither the test for chromium nor for ferrocyanide ions). $FeCy_6^{-4}$ was tested with ferric chloride and chromium by adding ammonium chloride and hydroxide. The observations are given below:

Volume of K_4FeCy_6 taken in each case = 1 c.c.
Strength of K_4FeCy_6 solution = 0.2 N
Strength of chromous chloride = 0.2615 N

Vol. of $CrCl_2$	Test for $FeCy_6^{-4}$	Test for Cr
0.80 c.c.	deep blue ppt.	No precipitate
0.90 c.c.	deep blue ppt.	No precipitate
1.00 c.c.	deep blue sol.	No precipitate
1.10 c.c.	light blue sol.	No precipitate
1.25 c.c.	slightly blue colour	No precipitate
1.20 c.c.	No blue colour	Slight ppt.
1.30 c.c.	No blue colour	Middle gelation ppt.
1.40 c.c.	No blue colour	Green gelation ppt.
1.50 c.c.	No blue colour	Green gelation ppt.
1.60 c.c.	No blue colour	Green gelation ppt.

It is from the above that a proportion of 1:1.20 gives almost a neutral sample of the complex. To get a more exact idea of the proportion experiment was performed with proportions ranging 1:1.6 and 1:2 and it was found that 1:1.17 ratio (K_4FeCy_6 ; $CrCl_2$) gave a neutral sample with its supernatant solution , giving neither the test for $FeCy_6^{-4}$ forchromium.

The following samples of the complex were prepared by mixing the reactants in different proportions in direct (i.e. chromous chloride to potassium ferrocyanide solution) and reverse order, in separate flasks(of 250 c.c. capacity). The reagents were thoroughly mixed and kept overnight and then filtered using Fichor universal centrifuge No. W346H at 5000 revolutions perminute. The following table gives the proportion and the order of mixing the reagents.

Sample	Ratio of K_4FeCy_6:$CrCl_2$ (by volume)	Manner of mixing
"A"	1 : 1.17	Chromous chloride
"B"	2 : 1.17	was added
"C"	1 : 2.34	K_4FeCy_6Direct additon
"D"	1 : 1.17	K_4FeCy_6 added to $CrCl_2$
"E"	1 : 1.17	Direct additions but washed with 10% alcohol

The samples 1 to 4 were washed repeatedly with water in the centrifuge itself till the filtrate no more gave the test for any ion (either Cl, K^+ Cr^{+++} or $FeCy_6^{-4}$). About 12 to 15 times washing was necessary except for the sample B(2:1) where excess of chromous chloride was used. In this case the filtrate became free of any ion after only four washings. In all the other cases and more so with sample "E" the precipitate showed tendency to pass through the filter paper in the colloidal form

(centrifuge running at 5000 revolutions per minutes). Sample E was washed in the begining with 10 % alcohol instead of water in order to suppress the hydrolysis if any. The filtration was quite slow and took 3-4 hours in every case.

The samples were dried over concentrated sulphuric acid in a vacuum dessicator and kept for further studies.

II. Some properties of the complex.

The following observations are made on the properties of the complex.

1. The complex has a colloidal nature as shown by:
   (a) The formation of jelly when chromous chloride is added to potassium ferrocyanide. (The gel structure is broken completely when it is disturbed).
   (b) Its passing into the filtrate in the form of very dilute sol when washed with water.
   (c) Its peptisability with excess potassium ferrocyanide and
   (d) The precipitate passing into sol by boiling a small quantity of it with large excess of water.
2. The complex does not go into solution in dilute and cold concentrated mineral acids and alkalis.
3. It is digested by boiling with concentrated sulphuric acid.
4. The coloursof various samples at different stages are tabulated below:

Sample	Colour in suspension	Colour after Filtration(still wet)	Colour after drying
A	Yellowish brown	Yellowish green	Dirty green
B	Dirty yellow	Yellowish green	Dirty yellow
C	Yellowish green	Light yellow	Yellowish green
D	Pea green	Yellow	Greyish black
E	Yellowish brown	Yellowish green	Dirty green

III. Analysis of the Complex.

Before proceeding with the analysis of the complex for its constituent elements, the water of hydration was first of all determined. The methods described below were used. Experiments in duplicate were carried out with each sample of the complex and the average values taken for the calculations.

Estimation of the water of hydration.

The water of hydration of the complex was determined by the simple ordinary methods of heating a known weight of the substance to 100°-110° . About 2 gm of the sample was heated to constant weight in an electric oven up to a temperature of 110° From the loss in weight, the percentage of water was calculated. The anhydrous complex was used for the chemical analysis.

Estimation of Iron.

The quantitative estimation of the different elements in the complex presented a number of difficulties due to the high stability of the complex. The alkali fusion was found to be the most satisfactory to break down the complex.

The weighed quantity (of about 0.4 to 0.5 gm.) of the anhydrous complex was mixed with about 3 to 4 gms, of pure sodium hydroxide and 2-3 gms. of sodium carborate (all these completely free from potassium). The whole mixture was made into a paste with few c.c. of water(to avoid spurting etc. on fusion) in a platinum dish and fused at the blow pipe. It was kept in the red hot molten state for about half an hour to ensure complete breakage of the complex. The following reaction takes place during the process.

$$\text{Complex} \xrightarrow[\text{fuse}]{NaOH + NaBO_2} Fe_2O_3 + Na_2CrB_4 + NaCN + KCN + KOH \text{ etc}$$

All the iron in the complex is converted to the oxide (or hydroxide), chromium into chromate, cyanogen into sodium or potassium cyanide, and potassium into cyanide or hydroxide. If any potssium or chloride ions were present in the complex in the adsorbed state, that will also be retained in some form or other. Only Fe_2O_3 remains in the solid state. After fusion the mass was cooled and then lixiviated with hot water. It was then filtered, the residue dissolved in warm dilute hydrochloric acid and precipitated with dilute ammonium hydroxide. This reprecipitation was carried out to remove the adsorbed chromate etc. completely. It was then filtered again and the precipitate used for the estimation of iron. Both the filtrates were collected and made up to 250 c.c. , and used for the estimation of chromium, potassium etc.

The gravimetric estimation of iron as Fe_2O_3 was tried first, but this was found to be time consuming and likely to bring in more errors. Hence the volumetric estimation was followed. The precipitated ferric hydroxide was dissolved in warm dilute sulphuric acid and the solution was made up to 100 c.c. in a volumetric flask. 250 c.c. of this solution was pipetted into a conical flask (of 100 c.c. capacity) and about 2 gms. of pure zinc dust and 20 c.c. of 4N sulphuric acidadded to it. The ferric iron got reduced to ferrous state by the nascent hydrogen. The contents were warmed to complete the reduction and after about 25-30 minutes, it was filtered, repeatedly washed and the collected filtrate was immediately titrated against standard potassium permanaganate solution. The method was found tobe quite satisfactory, giving concordant values.

A weighed quantity (0.3 - 0.5 gms) of the complex was made into paste with about 5 gms. of sodium hydroxide and 3 gms. of sodium peroxide and kept aside for 24 hours for complete digestion. It was then heated for a while, cooled and the mass lixiviated with water. The whole extract along with the ferric hydroxide precipitate was transferred to the flask of the quick fitting nitrogen estimation. The alkaline solution in the falsk was then acidified with 4 N sulphuric acid boiled for about two hours. The HCN gas evolved was absorbed in IN sodium hydroxide solution taken in the flask A, and made up to 250 c.c. in a volumetric flask. 250 c.c. of this solution was pipetted into a conical flask and titrated against standard silver nitrate solution using a few crystals of potassium iodide as indicator.

During the process of boiling with sulphuric acid some of the alkali cyanide hydrolysed to form ammonium sulphate. This nitrogen was estimated in the form of ammonia as follows.

After expelling the HCN, the contents were cooled and a concentrated solution of sodium hydroxide was then added to it and boiled to decompose the ammonium salt. The ammonia liberated was absorbed in 0.05 N sulphuric acid and the excess acid titrated back against standard alkali.

The total cyanogen thus calculated from the two data was checked up by calculating from the iron content in the complex, assuming that the ferrocyanogen group remains intact during the reaction. The two results were found totally well within experimental errors.

Estimation of chromium

Chromium which was present in the extract was estimated iodometrically using standard sodium thiosulphate. 25 c.c. of the extract (from 250 c.c. flask) was pipetted out into a conical flask and acidified in with 4 N sulphuric acid. About 1 gm. of potassium iodide was added to the above and the liberated iodine was titrated against thiosulphate solution using starch as indicator.

$$2\ Na_2CrO_4 + 5H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 2Na_2SO_4 + 5H_2O + 3O$$

$$3O + 6KI + 3H_2O \longrightarrow 6\ KOH + 3I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

The extract was highly alkaline and excess of acid had to be added for acidifying. The results were quite reproducible.

Estimation of potassium

The estimation of potassium as chloroplotinate is usually followed with much accuracy. But since this method is quite expensive and a large number of estimations had to be carried out, the cheap and equally accurate cobaltinitrite method[14] was preferred. The method is based on the fact that potassium is precipitated in the form of $K_2NaCo(NO_2)_6H_2O$ from a solution containing sodium Na and K in the ratio 22:1, by adding freshly prepared sodium cobaltinitrite. The precipitate is stable at 100°c. Since the extract already contained excess of Na, no fresh addition of it was found necessary.

28.0 gms. of cobalt was dissolved in a mixture of 75 c.c. of water and 25 c.c. of glacial acetic acid in a 500 c.c. flask.

A solution of 55 gms. of sidium nitrite in 100 c.c. of water was slowly added to the acetate solution. The whole mixture was warmed in the round bottomed flask and removed all the oxides of nitrogen by suction. It was then set aside for 24 hours, filtered to an Erlenmeyer flask, made up to 250 c.c. and kept in the dark. 25.0 c.c. of the extract, acidified with dilute acetic acid and about 25 c.c. of sodium cobaltinitrite solution added to it. The whole mixture was evaporated to dryness on an electric water bath. After cooling, the residue was lixivated with 5 % acetic acid, allowed the precipitate to settle and decanted through a weighed gooch crucible. It was washed repeatedly by decantation with the dilute acid, then transferred the lemon yellow precipitate to the crucible. The acetic acid was removed by final washings with distilled water and the precipitate was then dried at 100° to constant weight. From the weight of the sodium-potassium cobaltinitrite, the amount of potassium was calculated .

Since the potassium content was found to be very small in many cases, it was thought worthwhile to check the readings by calorimetric method. Lange's flame photometer model No.__ was used for the purpose. A calibration curve was first drawn with potassium chloride and the concentration of K in the sample was then directly read with the help of the curve. The results obtained by the two methods were found to agree very closely.

Estimation of CN:-

The estimation of nitrogen (or CN) was attempted by several methods. Kjeldahl's method[15] combined with Colman method[16] and used by L.C. Smith and Griswold[17] with slight modification was found to be the most satisfactory.

Chlorine:-

Qualitative tests were carried out with the extract to see whether any chlorine was present in the complex either in the adsorbed form or in any state of combination. There was no indication for the presence of any chloride ion in the extract.

Determination of the water hydration:-

The water of hydration of all the samples was determined simoultaneouslyand the anhydrous samples were used for chemical analysis . The readings for the percentage of water are given below:-

A

Sample	A	B	C	D	E
Wt. of complex before heating	2.134	2.0567	2.2143	2.0062	2.1817
Wt. of complex after heating	1.7830	1.5226	1.5058	1.3202	1.8426
Wt, of water	0.3520	0.5341	0.7085	0.6860	0.3391
Percentage of water	16.44	25.96	32.00	34.20	15.52

Analysis of the complex A.

The full details regarding the readings for the analysis of only one complex (A) are given as follows:-

Iron:

Weight of the substance taken for fusion	= 0.5120 gm.
Strength of $KMnO_4$ used for (standardised against 0.05 N oxalic acid)	= 0.026 N
Total volume of iron solution made up.	= 100 c.c.
Volume of solution taken for titration (after reduction etc.)	= 25.0 c.c.
Volume of $KMnO_4$ required for end point	= 14.95 c.c.

∴ Strength of ferrous solution $= \frac{14.95 \times 0.026}{25} = N$

Total iron present in the solution $= \frac{N \times 55.585}{10}$

∴ Percentage of the iron in the complex $= \frac{N \times 5.585 \times 100}{0.5120}$

$= \underline{16.94}$.

Chromium:-

(a) Standardisation of thiosulphate solution.

An exactly decinormal solution of potassium dichromate was prepared for the standardisation of the thiosulphate .

10 c.c. of the solution was pipetted out into a conical flask, added about 20 c.c. of dilute sulphuric acid and 1 gm. of solid potassium iodide and the liberated iodine was titrated against thiosulphate solution using starch as indicator. The readings are given below:-

Strength of dichromate = 0.1 N .

Volume of dichromate used = 10.0 c.c.

Volume of thiosulphate required = 10.2 c.c.

Strength of thiosulphate $= \frac{10 \times .1}{10.2} = 0.098$ N.

(b). Estimation of chromium:-

The extract, after the removal of iron was made upto 250 c.c.

Volume of the chromate solution used = 20.0 c.c.

Volume of thiosulphate = 3.7 c.c.

∴ Normality of chromate solution $= \frac{5.7 \times 0.098}{20}$ N

Equivalent wt. of chromium in the reaction $= \frac{Cr}{3} = \frac{52}{3}$

∴ Total wt. of chromium in the whole extract $= N \times \frac{52}{3} \times \frac{250}{1000}$

∴ Percentage of chromium in the complex $= N \times \frac{250}{1000} \times \frac{52}{3} \times \frac{100}{0.512}$

$= 23.65\%$

Percentage in the duplicate experiment = 23.71

∴ Average of the two values = 23.67 %

Potassium:-

20 c.c. of the extractwas used in each case for the precipitation of potassium. Two estimations were carried out simultaneously.

	I	II
Wt. Of Cobaltinitrite	= 0.0284 gm.	0.0281 gm.

Average weight = 0.0283 gm.

Molecular weight of $K_2NaCo(NO_2)_2 6H_2O$ = 454.1

454.1 gm. of cobaltinitrite ——— 78.2 gm. of K

∴ 0.283 gm. of cobaltinitrite ——— $\frac{78.2 \times 0.0283}{45411}$ gm.K.

Wt. of complex = 0.512 gm.

Total weight of K in the complex = $\frac{78.2 \times 0.0283}{454.1} \times \frac{250}{20}$

∴ Percentage of potassium in the complex = $\frac{78.2 \times 0.0283 \times 250 \times 100}{454.1 \times 20 \times 0.512}$

= 11.88 %

Percentage of K in the 2nd experiment. = 11.82 %

∴ The average percentage. = 11.85 %

Cyanogen:-

(a) Amount of CN evolved as HCN.

Strength of silver nitrate solution (determined against sodium chloride) = 0.05 N

Weight of the complex used = 0.4183 gm.

Total volume of the NaOH made up after absopption of HCN = 250 c.c.

Volume of the solution used for titration = 25 c.c.

Volume of $AgNO_3$ required = 8.45 c.c.

∴ Strength of NaCN solution = $\frac{8.45 \times 0.05}{25}$

Total weight of CN in the complex $= \frac{8.45 \times 0.05}{25} \times \frac{26}{4}$

$\therefore$ Percentage of CN $= \frac{8.45 \times 0.05 \times 26}{25 \times 4} \times \frac{100}{0.4183}$

$= \underline{26.25}$

(b) Amount of CN from the nitrogen evolved as ammonia:

Strength of sulphuric acid used for the absorption of ammonia $= 0.1$ N

Volume of acid used $= 100$ c.c.

Total volume made up after absorption $= 250$ c.c.

Volume used for each titration $= 50$ c.c.

Strength of NaOH used $= 0.055$ N.

Volume of NaOH required $= 12.15$ c.c.

$\therefore$ Strength of ammonia solution. $= \frac{12.15 \times 0.055}{50}$

Total weight of nitrogen in the whole solution. $= \frac{12.15 \times 0.055}{50} \times \frac{14}{4}$

$\therefore$ Amount of cyanogen equivalent $= \frac{12.15 \times 0.055}{50} \times \frac{26}{4}$

$\therefore$ Percentage of cyanogen $= \frac{12.15 \times 0.055 \times 26}{50 \times 4} \times \frac{100}{0.4183}$

$= 20.79$ %

(c) $\therefore$ Total percentage of cyanogen $= 47.04$ %

Total cyanogen calculated from the iron content.

55.85 gm. of iron ——— 156 gm. CN

16.94 gm. ——— $\frac{156 \times 16.94}{55.85} = 47.33$ CN

Hence the two values are found totally quite closely thereby showing the accuracy of the methods followed.

Estimation of potassium by flame photometer:

As a verification of the gravimetric method, the potassium content of the samples were also determined by Lang's flame photometer. The extract after removal of iron was used for the estimations. The flame photometer was first adjusted to a definite sensitivity

[illegible] was adjusted to zero. [illegible] was then atomised at a pressure of [illegible] atmosphere. The apparatus was then calibrated using standard solution of potassium chloride. The readings are given in the following table.

The [illegible] samples under test were then put for atomisation and the [illegible] readings obtained, the concentrations of potassium were calculated with the aid of the calibration graph.

S No.	Conc. of KCl	Deflection (d)	Log D	Deflection
1	N/200	80.0	1.9542	0.0111
2	N/300	74.5	1.8722	0.01243
3	N/400	55.0	1.7404	0.01813
4	N/500	47.0	1.6721	0.02128
5	N/1000	27.0	1.4314	0.0370
6	N/1500	20.0	1.3010	0.0500
7	N/2000	[illegible]	[illegible]	[illegible]
8	N/3000	7[illegible]	1.1761	0.03537

(Sensitivity factor of the apparatus 2)(vide calibration curve)

The curves 1 concentration x Dial reading (deflection)

The curves 11 concentration x Log dial reading

and 111 concentration x I/Dial reading

are plotted. The concentrations of K in the samples were calculated from the straight line plot of concentration against the reciprocal of dial reading (vide curve[illegible]). The readings are tabulated below:

S No.	Wt. of [illegible]	Dilution of extract	Dial reading (D)	I/D	[illegible] (from I/D)	Percentage
A	0.5[illegible]	[illegible]	80.0	0.0125	N/644	11.83
B	0.[illegible]	1000 c.c.	41.15	0.0243	N/256	23.23
C	0.4[illegible]	250 c.c.	"	"	"	"
D	0.6[illegible]	250 c.c.	"	"	"	"
E	0.5[illegible]	1000 c.c.	47.75	0.0205	N/[illegible]	1[illegible]

). Conductometric studies on chromous ferrocyanide complex.

It is a well known fact that precipitates, specially of those of complex compounds, change their nature and composition in passing from a freshly precipitated to the dry state. The method of chemical analysis suffers from the following drawbacks.

I. It fails to give definite composition to the precipitate; since in many cases, the composition of the precipitate changes with the concentration of the reactants and the nature of mixing.

II. In many cases, the changeof composition is actually due to the formation of more than one complex in successive stages during the mixing of the reactants. No idea can be obtained regarding this by chemical analysis.

III. No light is thrown on the exact nature and properties of the precipitate,

Physical methods, however, have been advantageously used to determine the composition of freshly precipitated compounds and also to get an insight into their nature. The electrometric methods like potentiometric and conductometric titrations have long been in use both in acid-bases and precipitation reactions. Conductometric method is not, however, well suited for oxidation reduction reactions since in the majority of cases the solution must necessarily contain relatively large concentrations of acid or base which more or less completely mask the change in conductance due to redox reductions. The method has not yet been utilised as fully as it should be in practical analysis due to the wrong idea that it is applicable to solutions containing foreignelectrolytes Actually, these drawbacks can be rectified by using high precision resistance bridge.

ESTIMATION OF POTASSIUM By FLAME PHOTO

Curves I II III

I Concentration × Deflection

II " × log D

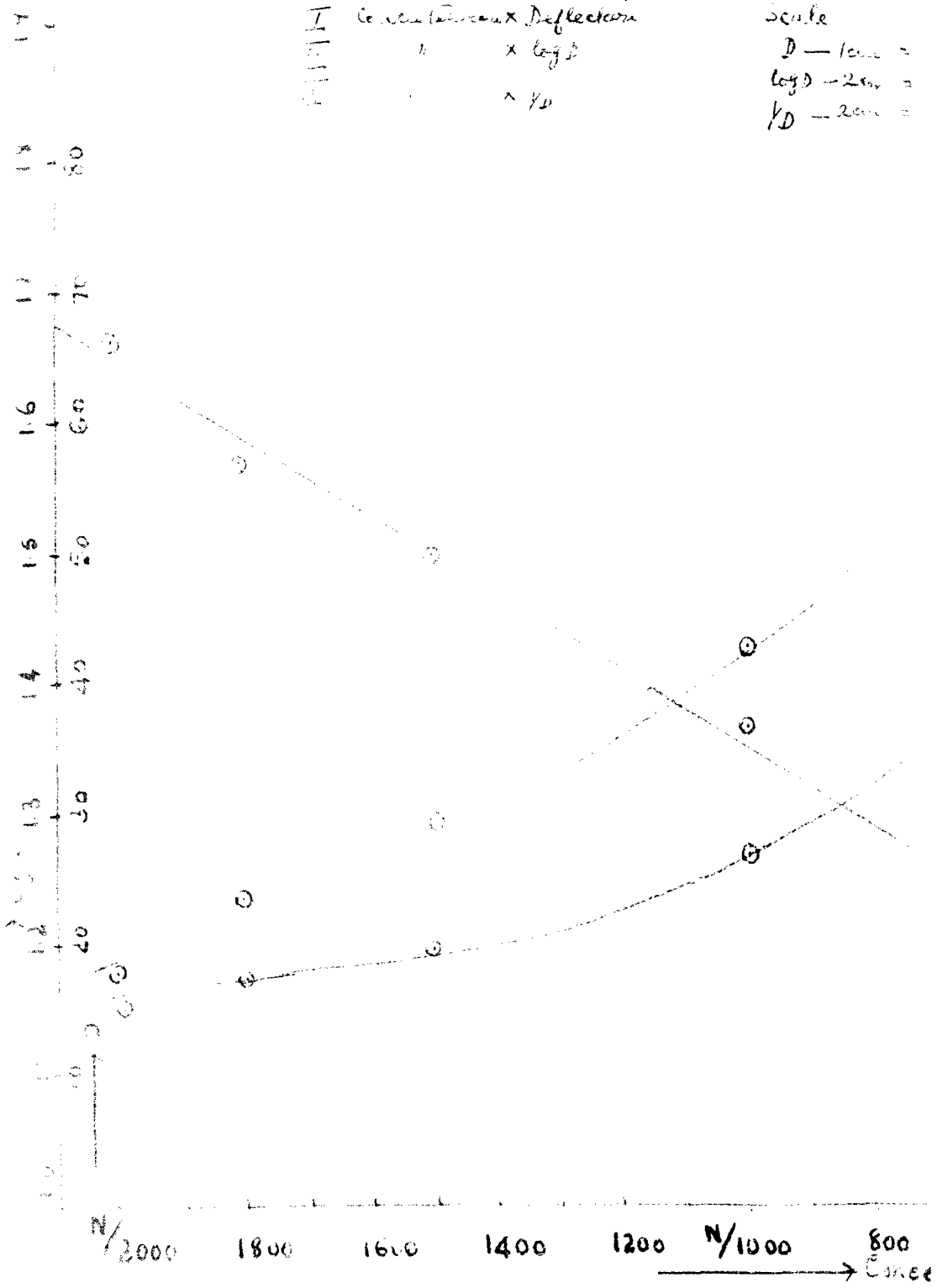
III " ∝ γ_D

Scale

D — 1cm =

log D — 2cm =

γ_D — 2cm =



The samples 'C' and 'D' gave a very small deflection even with original dilutions(i.e.250 c.c.) and with the maximum sensitivity of the apparatus. The results were found to agree with those obtained by the gravimetric method.

Analysis of the other samples 'B' to 'E'.

The analysis of all other samples were also carried out exactly in a similar way as described in the foregoing pages. The details regarding the calculations are not given since the method has already been illustrated in detail for the analysis of the complex'A'. The results are given below:

TABLE B.

Complex Sample	Expt. No.	Percentage constituents. K	Cr	Fe	CN
B	1	26.21	12.46	16.09	45.04
	2	26.27	12.52	16.13	44.98
Average		26.24	12.49	16.11	44.01
C	1	negligible	32.84	16.46	46.10
	2	beyond	32.03	16.50	45.92
Average		estimation	32.98	16.48	46.01
D	1	negligible	32.88	17.61	49.31
	2	beyond	32.92	17.70	49.42
Average		estimation	32.90	17.66	49.37
E	1	13.38	22.41	16.84	47.05
	2	13.52	22.49	16.92	47.21
Average		13.45	22.45	16.88	47.13

Calculation of the Empirical formula.

From the percentage composition obtained by analysis, the empirical formula of the complex was calculated. Since the anhydrous sample was used for the analysis, the water content was calculated

separetely and tabulated accounlingly. The calculation of the empirical formula is summarised in the following table.

TABLE C.

Sample	Constituent	Percentage	Equivalent	Ratio
A	K	11.85	0.3038	1.001
	Cr	23.67	0.4552	1.501
	Fe	16.94	0.3034	1
	CN	47.33	1.821	6.002
B	K	26.24	0.6726	2.801
	Cr	12.49	0.2402	1
	Fe	16.11	0.2885	1.201
	CN	44.01	1.692	7.049
C	K	-	-	-
	Cr	32.98	0.6343	2.150
	Fe	16.48	0.2950	1
	CN	46.01	1.770	5.998
D	K	-	-	-
	Cr	32.90	0.6327	2.001
	Fe	17.66	0.3162	1
	CN	49.37	1.899	6.003
E	K	13.45	0.3447	1.140
	Cr	22.45	0.4317	1.429
	Fe	16.88	0.3023	1
	CN	47.13	1.812	5.996

Hence the empirical formulae are:

'A' ———	K	Cr	Fe	(CN)	(1)
	1.001	1.501	1	6.002	
'B' ———	K	Cr	Fe	(CN)	(2)
	2.801	1	1.201	7.049	
'C' ———	K	Cr	Fe	(CN)	(3)
		2.15	1	5.998	
'D' ———	K	Cr	Fe	(CN)	(4)
		2.001	1	6.003	
'E' ———	K	Cr	Fe	(CN)	(5)
	1.14	1.429	1	5.996	

Molecular formula of the complex.

The molecular formula of different samples of the complex can be written as:

'A' Multiply 1 by 2 $K_2Cr_3[Fe(CN)_6]_2$.

'B' $K_2CrFe(CN)_6.0.2K_4Fe(CN)_6$.

'C'* $Cr_2Fe(CN)_6.0.08Cr_2O_3$.

'D' $Cr_2Fe(CN)_6$.

'E' Multiply 5 by 2 $K_2Cr_3[Fe(CN)_6]_2\ 0.1K_4Fe(CN)_6$.

* In the case of this sample the total percentage of the constituents by estimation was quite low (95.5%), and the chromium content was high. Hence this excess chromium was accounted for to be present as Cr_2O_3 in the chromous complex.

Assuming the molecular formulae of the complexes to be one or the other of the above (neglecting the Cr and $FeCy_6$ adsorbed) the number of molecules of water was calculated in each case from the percentage of water as given below.

TABLE D.

Sample	Mole.formula of complex	Calculated Mol. Wt.	percentage of water	No. of Mole. of water
'A'	$K_2Cr_3[Fe(CN)_6]_2$	587.7	18.44	3.007 (3)
'B'	$K_2CrFe(CN)_6$	342	25.93	4.932 (5)
'C'	$Cr_2Fe(CN)_6$	313	34.20	5.616 (6)
'D'	$Cr_2Fe(CN)_6$	313	34.20	6.000 (6)
'E'	$K_2Cr_3[Fe(CN)_6]_2$	667.5	15.5	5.671 (6)

The number of molecules of water is found to be 6 in all cases except for sample 'B'. Hence the formulae of the complex can now be written as:

1. $K_2CrFe(CN)_6.5H_2O$.

2. $Cr_2Fe(CN)_6.6H_2O$.

3. $K_2Cr_3[Fe(CN)_6]_2.6H_2O$. or $K_2CrFe(CN)_6.Cr_2Fe(CN)_6.6H_2O$

Inference and short discussion.

The chemical analysis of chromous ferrocyanide obtained by mixing potassium ferrocyanide and chromous chloride in different proportion, lead to the following conclusions:

1. The composition of the complex depends on the proportion, of the reagents, and the manner of mixing(i.e. potassium ferrocyanide added to chromous chloride or vice versa), and hence the complex could not be assigned one simple formula to represent its composition .

2. The analysis of samples 'C' and 'D' (obtained by mixing potassium ferrocyanide and chromous chloride in the ratio 1:2.34 and 1:1.17 respectively) show that a complex of definite composition $Cr_2Fe(CN)_6$ is formed when large excess of chromous chloride is added to potassium ferrocyanide or when the mixing is carried out in the reverse order.

3. It is interesting to note that the total percentage of the elements obtained by analysis of 'C' is too low and cannot be accounted for as experimental error. Moreover the chromium content is also high. This disparity in the percentage and the presence of excess of chromium can be explained as follows:

Since the sample is precipitated in presence of very large excess of chromous chloride, it is evident that some of the latter will remain adsorbed. This adsorbed chromous chloride gets oxidised to the chromic state on exposure to air. Much of this adsorbed Cr(III)

cyanide was retained in the absorbed state. This is possibly due to the very low solubility of K_4FeCy_3 in alcohol.

8. The potassium chloride which is found as product of the reaction

is removed by repeated washing and the rest which still remains gets hydrolysed to give the hydroxide. During dehydration (since anhydrous samples were used for analysis), this hydroxide changes to the oxide, $Cr^{\circ\circ\circ} \longrightarrow Cr(OH)_3 \longrightarrow Cr_2O_3$. The disparity in the percentage is due to the oxygen of Cr_2O_3 and the high value for chromium is due to the adsorptium property of the complex.

4. The sample 'D' obtained by mixing potassium ferrocyanide to chromous chloride (ratio 1:1·17) gives the neutral complex $Cr_2Fe(CN)_6$ without any excess of either chromium or ferrocyanide.

5. When chromous chloride is added to excess potassium ferrocyanide sample 'B' (ratio 2:1·17), the complex formed has the composition $K_2CrFe(CN)_6$, one $Cr^{\circ\circ}$ replacing two potassium ions. The excess of potassium ferrocyanide is not completely washed off, some of it remains irreversible adsorbed and this is found to be 0.2 mole. per mole of the complex. This points towards the capacity of high adsorption of the complex.

6. The analysis of the samples 'A' and 'E' obtained by mixing chromous chloride to potassium ferrocyanide (in the ratio 1:1·17) gives the composition K Cr Fe(CN) . This is possibly a mixture of $K_2Cr_3Fe(CN)_6$ —(i) and $Cr_2Fe(CN)_6$ —(ii). In the beginning complex (i) is formed, but when the proportion of chromous chloride exceeded ratio, it is gradually converted to complex (ii). This is quite plausible as seen from the analysis of sample 'C'. Hence the composition can better be written as $K_2Cr_3Fe(CN)_6$.

7. In the case of sample 'A' the excess ferrocyanide could almost

cyanide was retained in the absorbed state. This is possibly due to the very low solubility of K_4FeCy_6 in alcohol.

8. The potassium chloride which is formed as product of the reaction is completely washed off. No detectable amount of Cl was found in any sample.

9. The number of molecules of H_2O associated with one mole of the complex is is 6 (except with sample 'B' —$K_2CrFe(CN)_6$ where it is found to be 5).

10. The overall reaction taking place between chromous chloride and potassium ferrocyanide may be given as:

(i). $K_4Fe(CN)_6 + CrCl_2 \longrightarrow K_2CrFe(CN)_6 + 2KCl$

(ii). $K_4Fe(CN)_6 + 2CrCl_2 \longrightarrow Cr_2Fe(CN)_6 + 4\ KCl$

(iii). $2K_4Fe(CN)_6 + 3CrCl_2 \longrightarrow K_2Cr_3[Fe(CN)_6]_2 + 6\ KCl$

-:0:-

In spite of all this, the method has taken an important place in the physico-chemical studies of the nature and composition of both the soluble and insoluble complexes, specially when the complex formation takes place in two or more successive stages and where phenomena like hydrolysis and adsorption play important roles. The principle of conductometric method, in brief, is as follows:

The electrical conductance of a solution is a summation of contributions from all the ions present and hence, is not a specific property of any particular ionic species, as the potential of an indicator electrode is. If a solution contains a mixture of two salts A_1B_1 and A_2B_2 which are dissociated into the ions $A_1A_2B_1$ and B_2 There are, in general, many values for the concentrations c_1 of A_1, B_1 and c_2 of A_2 B_2 which will give the same observed conductance in a given cell. Without other informations, the concentration c_1 and c_2 cannot be computed from the measured conductance. If, however, the concentrations of all other salts except A_1, B_1 are kept constant then the observed conductance can be related to c_1. This is the principle involved in conductometric titrations and analysis.

Since a solid complex is formed by the interaction of potassium ferrocyanide and chromous chloride, the principle of precipitation titration can be successfully used. The precipitation titration of a cation A of a salt AB by the anion B of a salt MB (say the cation Cr^{++} of $CrCl_2$ by the anion $Fe(CN)_6^{4-}$ of potassium ferrocyanide) may be represented by

$$M^+ + A^- + M^+ + B^- \rightleftharpoons MB(s) + M^+ + A^-$$

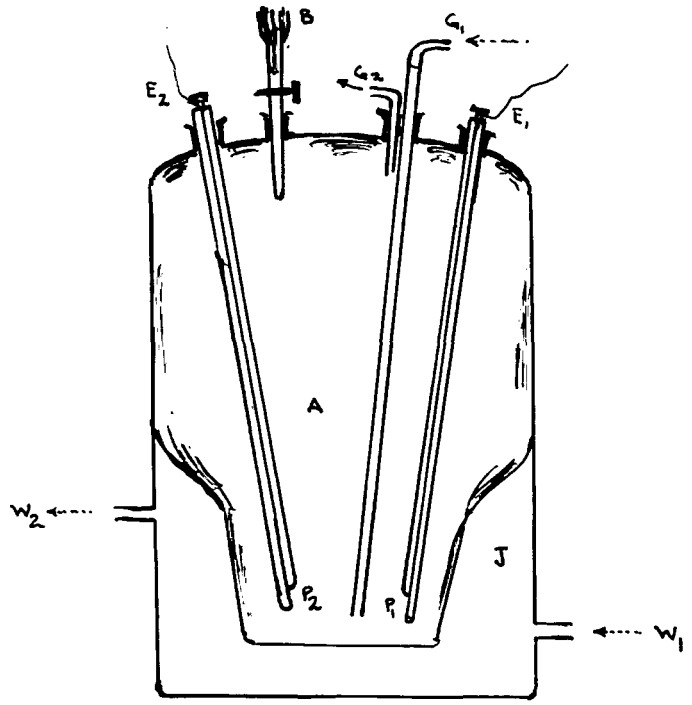
the result being the replacement of a cation M°with M: M: M :: M then the conductance remains constant up to the end point, and increases beyond that Gue to excess MD to yield a titration curve like ⌊/. If $\lambda M > \lambda M$ the titration curve will be ⩽/, and $\lambda M < \lambda N$, it will have the shape /. Since V shaped curves tend to give the most precise results it is advantageous to employ a titrant salt corresponding to $\lambda M > \lambda M$.

In view of the fact that valuable information regard·· could be obtained by ing the nature and composition of the precipitate/conductivity results, this method was employed for this complex.

(a). Preparation of reagents: Pure chromous chloride and potassium ferrocyanide solutions were prepared and standardised as described earlier. The strength of potassium ferrocyanide was adjusted, according to need by diluting with conductivity water, since the dilution of chromous chloride, being inconvenient in the measure flask it was brought about in the titration cell it-self, whenever required, by transferring calculated volume and making up with water (this was necessary when chromous chloride was used as titrating solution).

(b). Apparatus and Procedure: The titrations were carried out using a [illegible] conductivity bridge and a jacket type conductivity cell. The four [illegible] cell (Fig .6) is of 100 c.c. capacity [illegible] jacket J for water circulation to maintain a constant temperature. W and W are the inlet and outlet respectively for the jacket. Two platinum electrodes

FIG. 6



A... CONDUCTIVITY CELL

J... JACKET

W_1, W_2— WATER INLET AND OUTLET

E_1, E_2— ELECTRODE CARRIERS WITH GROUND GLASS JOINT

P_1, P_2— PLATINUM ELECTRODES COATED WITH PLATINUM BLACK

G_1, G_2— N_2 INLET AND OUTLET

B... MICROBURETTE

P_1 P_2 of about 0.75 sq.cm. each and coated with platinum black are kept in a fixed position about 3 cm. apart by the electrode carriers $E_1$and E_2 provided with ground joints. The nozle of of the microburette (attached to the storage flask when $CrCl_2$ is the titrant or a separate oneof 2 c.c. capacity when ferrocyanide is the titrant) is inserted through a rubber stopper fitted in the third neck. The fourth neck and outlet of the cell is fitted with a rubber cork carrying and inlet and outlet for nitrogen which is used to produce inert atmosphere. The outlet for the gas carries a Bunsen valve arrangement . Nitrogen from pressure cylinder is purified by passing through washers.

A volume of the titrating solution enough to keep the elctrodes completely immersed, was taken in the cell and aliquots of the titrant added the microburette . Readings were taken after completemixing by the current of nitrogen(which served the double purpose of mixing and keeping the inert atmosphere).

(1). Direct titrations- potassium ferrocyanide in the cell. Calculated amount to give the desired concentration was taken in the cell and the volume made up to 25 c.c. with conductivity water. The air in the cell was then completely displaced by continuously bubbling the nitrogen for about half an hour. Water at constant temperature was circulated through the jacket. After complete displacement of air, aliquote of chromous chloride were added, and readings taken after complete mixing. The current of nitrogen was stopped at the time of taking reading. The

titrations were carried out with different concentrations of potassium ferrocyanide and also in presence of aclcohol.

(ii). Reverse titrations: Chromous chloride in the cell. For carrying out the reverse titrations, quantity of water which would make up a total volume of 25 c.c. after the addition of chromous chloride calculated to give the necessary strength, was taken in the cell and the current of nitrogen passed through it. When the dissolved air and the air in the cell was completely removed (in about 30 minutes time) chromous chloride solution was added to it. The titration was then continued taking readings after adding increasing amount of potassium ferrocyanide. The titrations were carried out with different concentrations of chromous chloride and also in presence of alcohol in order to see the influence of the latter on the titre value.

(iii). Volume correction: The conductance of a solution vary greatly with dilution and hence in order to get accurate results a correction for the volume of the titrant added, is to made[18,19] To minimise this error due to increase in volume it is recommended that the titrant should be at least 50 times as concentrated as the solution to be titrated so that the total volume in the cell does not increase considerably at the end of the reaction. The specific conductivity of any electrolyte veing roughly proportional to this coneentration, the observed conductivity of the mixed reactants of total volume, say(V+v c.c.) was multiplied by $\frac{V+v}{V}$ at each stage of mixing where V refer to the volume of the reactant originally taken in the cell.

The readings for the direct and reverse titrations are tabulated as follows. A temperature of 18 $\pm$ 0.5° was maintained in all titrations.

Readings for the direct titrations:

TABLE CLXV

Volume of 0.2 M $K_4Fe(CN)_6$ = 1.25 c.c.
Volume of alcohol = 0.0 c.c.
Total volume made up=25 c.c.
∴ Conc. of $K_4Fe(CN)_6$=0.01 N
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$ added	Conductance	corrected conductance
0.0 c.c.	1.67×10^{-2}	1.67×10^{-2}
0.2 "	1.62 "	1.63 "
0.3 "	1.59 "	1.61 "
0.4 "	1.57 "	1.60 "
0.5 "	1.55 "	1.58 "
0.6 "	1.57 "	1.57 "
0.7 "	1.59 "	1.64 "
0.8 "	1.60 "	1.65 "
0.9 "	1.63 "	1.69 "
1.0 "	1.65 "	1.72 "
1.1 "	1.66 "	1.73 "
1.2 "	1.70 "	1.78 "
1.3 "	1.75 "	1.84 "
1.4 "	1.80 "	1.90 "
1.5 "	1.92 "	2.04 "

(Vide curve No. 145)

i) 250 c.c. 0.01 M $K_4Fe(CN)_6$
= 0.5 c.c. of 0.45 M $CrCl_2$
= 22.7 c.c. of 0.01 M $CrCl_2$

ii)1265 c.c. of 0.45M $CrCl_2$
= 47.67 c.c. 0.01 M $CrCl_2$

TABLE CLXVI

Volume of 0.2 M $K_4Fe(CN)_6$= 1.25cc.
Volume of alcohol = 20 c.c.
Total volume made up = 25 c.c.
∴ Conc. of $K_4Fe(CN)_6$= 0.01 N
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$ added	Conductance	Corrected conductance
0.0 c.c.	1.57×10^{-2}	1.57×10^{-2}
0.2 "	1.62 "	1.63 "
0.3 "	1.63 "	1.65 "
044 "	1.62 "	1.65 "
0.5 "	1.60 "	1.63 "
0.6 "	1.62 "	1.66 "
0.8 "	1.67 "	1.72 "
1.0 "	1.72 "	1.79 "
1.1 "	1.72 "	1.80 "
1.2 "	1.75 "	1.83 "
1.3 "	1.80 "	1.89 "
1.4 "	1.83 "	1.93 "
1.5 "	1.88 "	1.99 "

(Vide curve No. 146)

i) 25 c.c. 0,01 M $K_4Fe(CN)_6$
= 0.53 c.c. 0.45 M $CrCl_2$
= 24.06 c.c. 0.01 M $CrCl_2$

ii) 1.06 c.c. 454 M $CrCl_2$
= 47.12 c.c. 0.01 M $CrCl_2$

TABLE CLXVII

Volume of 0.2 M K_4FeCy_6 = 1.25 c.c.
Volume of alcohol = 5.0 c.c.
Total volume made up = 25.0 c.c.
∴ Conc. of K_4FeCy_6 = 0.01 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	1.54 x 10^{-2}	1.54 x 10^{-2}
0.2 "	1.65 "	1.66 "
0.3 "	1.68 "	1.70 "
0.4 "	1.69 "	1.72 "
0.5 "	1.67 "	1.70 "
0.6 "	1.67 "	1.70 "
0.8 "	1.73 "	1.79 "
0.9 "	1.76 "	1.82 "
1.0 "	1.80 "	1.88 "
1.2 "	1.83 "	1.92 "
1.3 "	1.85 "	1.95 "
1.5 "	1.90 "	2.02 "

(Vide curve No. 147)

i) 25 c.c. 0.01 M K_4FeCy_6
= 0.55 c.c. 0.454 $CrCl_2$
= 24.97 c.c. 0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6
= 1.08 c.c. 0.454 M $CrCl_2$
= 59.03 c.c. 0.01 M $CrCl_2$

TABLE CLXVIII

Volume of 0.2 M K_4FeCy_6 = 2.5 c.c.
Volume of alcohol = 0.0 c.c.
Total volume made up = 25.0 c.c.
∴ Conc. of K_4FeCy_6 = 0.02 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	1.85 x 10^{-2}	1.85 x 10^{-2}
0.2 "	1.80 "	1.81 "
0.4 "	1.74 "	1.77 "
0.6 "	1.70 "	1.74 "
0.8 "	1.65 "	1.70 "
1.0 "	1.60 "	1.66 "
1.2 "	1.63 "	1.71 "
1.4 "	1.67 "	1.76 "
1.8 "	1.75 "	1.88 "
2.0 "	1.80 "	1.95 "
2.2 "	1.82 "	1.98 "
2.4 "	1.88 "	2.06 "
2.6 "	1.92 "	2.12 "

(Vide curve No. 148)

i) 25 c.c. 0.02 M K_4FeCy_6
= 1.03 c.c. 0.454 $CrCl_2$
= 23.38 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 2.1 c.c. 0.454 M $CrCl_2$
= 47.67 c.c. 0.02 M $CrCl_2$

TABLE CLXIX

Volume of 0.2 M K_4FeCy_6 = 2.5 c.c.
Volume of alcohol = 2.0 c.c.
Total volume made up = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.02 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	1.68×10^{-2}	1.68×10^{-2}
0.2 "	1.72 "	1.73 "
0.4 "	1.74 "	1.77 "
0.6 "	1.74 "	1.80 "
0.8 "	1.71 "	1.77 "
1.0 "	1.67 "	1.74 "
1.2 "	1.71 "	1.79 "
1.4 "	1.74 "	1.86 "
1.6 "	1.78 "	1.90 "
1.8 "	1.81 "	1.94 "
2.0 "	1.85 "	2.00 "
2.2 "	1.85 "	2.06 "
2.4 "	1.86 "	2.08 "
2.6 "	1.92 "	2.12 "

(Vide curve No. 149)

i) 25 c.c. of 0.02 M K_4FeCy_6
= 1.06 c.c. 0.454 $CrCl_2$
= 24.06 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. of 0.02 M K_4FeCy_6
= 2.06 c.c. 0.454 $CrCl_2$
= 46.75 c.c. 0.02 M $CrCl_2$

TABLE CLXX

Volume of 0.2 M K_4FeCy_6 = 2.5 c.c.
Volume of alcohol = 50 c.c.
Total volume made up = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.02 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	1.60×10^{-2}	1.60×10^{-2}
0.2 "	1.70 "	1.71 "
0.4 "	1.77 "	1.80 "
0.6 "	1.82 "	1.86 "
0.8 "	1.82 "	1.88 "
1.0 "	1.80 "	1.87 "
1.2 "	1.78 "	1.87 "
1.4 "	1.80 "	1.90 "
1.6 "	1.85 "	1.97 "
1.8 "	1.90 "	2.04 "
2.0 "	1.92 "	2.07 "
2.2 "	1.95 "	2.12 "
2.4 "	1.98 "	2.18 "
2.6 "	2.00 "	2.21 "

(Vide curve No. 150)

i) 25 c.c. 0.02 M K_4FeCy_6
= 1.1 c.c. 0.454 $CrCl_2$
= 24.91 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 1.9 c.c. 0.454 M $CrCl_2$
= 43.1 c.c. 0.02 M $CrCl_2$

TABLE CLXXI

Volume of 0.2 M K_4FeCy_6 = 3.75 c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.03 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	2.78×10^{-2}	2.78×10^{-2}
0.5 "	2.68 "	2.74 "
0.7 "	2.65 "	2.72 "
1.0 "	2.60 "	2.70 "
1.3 "	2.55 "	2.68 "
1.5 "	2.52 "	2.67 "
1.7 "	2.55 "	2.72 "
2.0 "	2.57 "	2.78 "
2.5 "	2.63 "	2.89 "
3.0 "	2.70 "	3.03 "
3.2 "	2.70 "	3.05 "
3.5 "	2.72 "	3.10 "
3.8 "	2.78 "	3.20 "
4.0 "	2.82 "	3.27 "
4.5 "	2.90 "	3.42 "
5.0 "	3.05 "	3.60 "

(Vide curve No. 151)

1) 25 c.c. 0.03 M K_4FeCy_6
= 1.5 c.c. 0.454 M $CrCl_2$
= 22.55 c.c. 0.03 M $CrCl_2$

11) 25 c.c. 0.03 M K_4FeCy_6
= 3.15 c.c. 0.454 M $CrCl_2$
= 47.56 c.c. 0.03 M $CrCl_2$

TABLE CLXXII

Volume of 0.2 M K_4FeCy_6 = 3.75 c.c.
Volume of alcohol = 2.0 c.c.
Total volume = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.03 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	2.55×10^{-2}	2.55×10^{-2}
0.5 "	2.65 "	2.70 "
0.7 "	2.68 "	2.75 "
1.0 "	2.70 "	2.81 "
1.3 "	2.70 "	2.84 "
1.5 "	2.68 "	2.84 "
1.7 "	2.67 "	2.85 "
2.0 "	2.70 "	2.92 "
2.5 "	2.73 "	3.00 "
3.0 "	2.75 "	3.08 "
3.2 "	2.76 "	3.11 "
3.5 "	2.78 "	3.17 "
3.8 "	2.80 "	3.23 "
4.0 "	2.82 "	3.27 "
4.5 "	2.87 "	3.39 "
5.0 "	2.93 "	3.52 "

(Vide curve No. 152)

1) 25 c.c. 0.03 M K_4FeCy_6
= 1.6 c.c. 0.454 M $CrCl_2$
= 24.16 c.c. 0.03 M $CrCl_2$

11) 25 c.c. 0.03 M K_4FeCy_6
= 3.1 c.c. 0.454 M $CrCl_2$
= 46.8 c.c. 0.03 M $CrCl_2$

CONDUCTOMETRIC TITRATIONS BETWEEN $CrCl_2$ and $K_4Fe(CN)_6$ (Conc. 1/4)

(Direct $K_4Fe(CN)_6$ in the cell)

CURVES 145 & 156

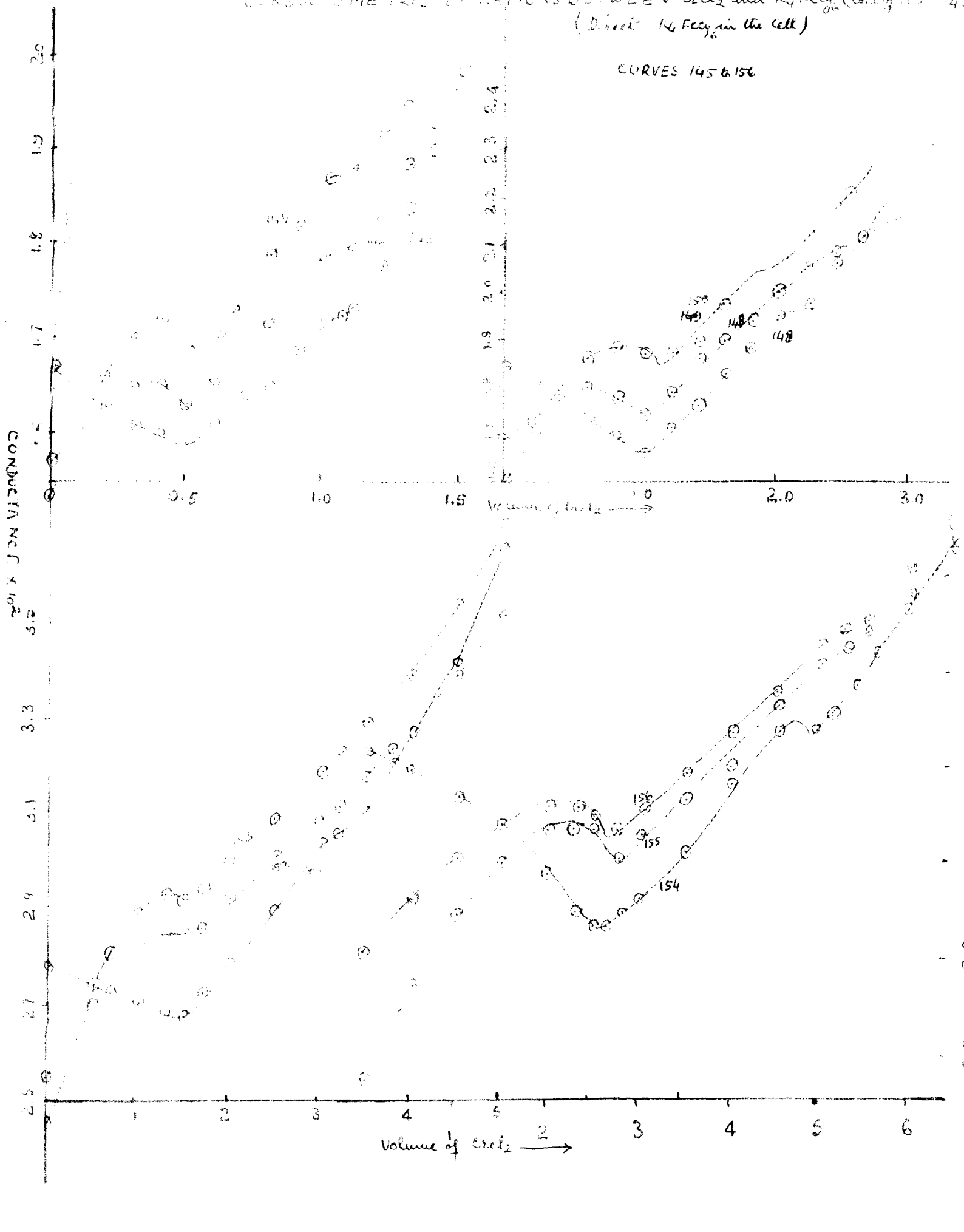


TABLE CLXXXIV

Volume of 0.2 M K_4FeCy_6 = 3.75 c.c.
Volume of alcohol = 5.0 c.c.
Total volume = 25.0 c.c.
∴ Conc. of K_4FeCy_6 = 0.03 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	2.45 x 10^{-2}	2.45 x 10^{-2}
0.5 "	2.65 "	2.70 "
0.7 "	2.72 "	2.80 "
1.0 "	2.78 "	2.89 "
1.3 "	2.80 "	2.92 "
1.5 "	2.75 "	2.91 "
1.7 "	2.75 "	2.94 "
2.0 "	2.77 "	3.00 "
2.5 "	2.80 "	3.03 "
3.0 "	2.82 "	3.17 "
3.2 "	2.85 "	3.22 "
3.5 "	2.85 "	3.28 "
4.0 "	2.82 "	3.39 "
4.5 "	3.00 "	3.54 "
5.0 "	3.08 "	3.61 "

(Vide curve No. 153)

1) 25 c.c. 0.03 M K_4FeCy_6
= 1.03 c.c. 0.454 M $CrCl_2$
= 24.6 c.c. 0.03 M $CrCl_2$

2.) No clear break

TABLE CLXXXV

Volume of 0.2 M K_4FeCy_6 = 6.25 c.c.
Volume of alcohol = 5.0 c.c.
Total volume = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.05 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	3.23 x 10^{-2}	3.23 x 10^{-2}
0.5 "	3.13 "	3.19 "
0.8 "	3.00 "	3.12 "
1.5 "	2.90 "	3.07 "
2.0 "	2.75 "	3.07 "
2.3 "	2.65 "	3.00 "
2.5 "	2.60 "	2.95 "
2.8 "	2.60 "	2.99 "
3.0 "	2.61 "	3.02 "
3.5 "	2.65 "	3.08 "
4.0 "	2.72 "	3.15 "
4.5 "	2.78 "	3.28 "
5.0 "	2.81 "	3.39 "
5.3 "	2.80 "	3.42 "
5.5 "	2.80 "	3.42 "
6.0 "	2.85 "	3.53 "
6.5 "	2.92 "	3.68 "

(Vide curve No. 154)

1) 25 c.c. 0.05 M K_4FeCy_6
= 2.8 c.c. 0.454 M $CrCl_2$
= 23.61 c.c. 0.05 M $CrCl_2$

2) 25 c.c. 0.05 M K_4FeCy_6
= 4.8 c.c. 0.454 M $CrCl_2$
= 43.6 c.c. 0.05 M $CrCl_2$

TABLE CLXXV

Volume of 0.2 M K_4FeCy_6 = 6.25 c.c.
Volume of alcohol = 2.0 c.c.
Total volume = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.05 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected Conductance
0.0 c.c.	2.80 x 10^{-2}	2.80 x 10^{-2}
0.5 "	2.85 "	2.81 "
1.0 "	2.88 "	2.80 "
1.5 "	2.90 "	2.87 "
2.0 "	2.88 "	2.81 "
2.5 "	2.85 "	2.81 "
3.0 "	2.82 "	2.80 "
3.5 "	2.75 "	2.63 "
4.0 "	2.78 "	2.71 "
4.5 "	2.80 "	2.79 "
5.0 "	2.82 "	2.87 "
5.5 "	2.85 "	2.93 "
6.0 "	2.88 "	2.98 "
6.5 "	2.82 "	2.91 "
7.0 "	2.85 "	2.92 "
7.5 "	2.85 "	2.92 "

(Vide curve No. 155)

1) 25 c.c. 0.05 M K_4FeCy_6
= 2.65 c.c. 0.454 M $CrCl_2$
= 24.03 c.c. 0.05 M $CrCl_2$

11) 25 c.c. 0.05 M K_4FeCy_6
= 5.3 c.c. 0.454 M $CrCl_2$
= 48.1 c.c. 0.05 M $CrCl_2$

TABLE CLXXVI

Volume of 0.2 M K_4FeCy_6 = 6.25 c.c.
Volume of alcohol = 5,0 c.c.
Total volume = 25 c.c.
∴ Conc. of K_4FeCy_6 = 0.05 M
Strength of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Conductance	Corrected conductance
0.0 c.c.	2.55 x 10^{-2}	2.55 x 10^{-2}
0.5 "	2.58 "	2.73 "
1.0 "	2.77 "	2.84 "
1.5 "	2.82 "	2.90 "
2.0 "	2.83 "	3.03 "
2.5 "	2.80 "	3.05 "
3.0 "	2.73 "	3.05 "
3.5 "	2.70 "	3.00 "
4.0 "	2.72 "	3.05 "
4.5 "	2.75 "	3.13 "
5.0 "	2.75 "	3.20 "
5.5 "	2.82 "	3.38 "
6.0 "	2.85 "	3.42 "
6.5 "	2.88 "	3.49 "
7.0 "	2.89 "	3.57 "
7.5 "	2.80 "	3.33 "

(Vide curve No. 153)

1) 25 c.c. 0.05 M K_4FeCy_6
= 2.75 c.c. 0.454 M $CrCl_2$
= 24.97 c.c. 0.05 M $CrCl_2$

11) Not well defined

Reverse titration ——$CrCl_2$ in the cell.

TABLE CLXXVII

Volume of 0.454 M $CrCl_2$ = 0.05 c.c.

Volume of alcohol = 0.0 c.c.

Total volume = 25 c.c.

∴ Conc. of $CrCl_2$ = 0.0091 M

Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	1.03 x 10^{-2}	1.03 x 10^{-2}
0.2 "	0.99 "	1.00 "
0.3 "	0.97 "	0.98 "
0.4 "	0.96 "	0.98 "
0.5 "	0.95 "	0.97 "
0.6 "	0.97 "	0.99 "
0.7 "	1.01 "	1.04 "
0.8 "	1.06 "	1.09 "
1.0 "	1.10 "	1.14 "
1.1 "	1.07 "	1.14 "
1.2 "	1.09 "	1.14 "
1.3 "	1.12 "	1.18 "
1.4 "	1.16 "	1.23 "
1.5 "	1.22 "	1.29 "

(Vide curve No. 157)

i) 25 c.c. 0.009 M $CrCl_2$

= 0.56 c.c. 0.2 M K_4FeCy_6

= 11.3 c.c. 0.009 M

ii) 25 c.c. 0.009 M $CrCl_2$

= 11.3 c.c. 0.2 M K_4FeCy_6

= 25.1 c.c. 0.009 M K_4FeCy_6

TABLE CLXXVIII

Volume of 0.454 M $CrCl_2$ = 0.5 c.c.

Volume of alcohol = 5.0 c.c.

Total volume = 25 c.c.

∴ Conc. of $CrCl_2$ = 0.0091 M

Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	0.82 x 10^{-2}	0.82 x 10^{-2}
0.2 "	0.81 "	0.82 "
0.3 "	0.81 "	0.82 "
0.4 "	0.81 "	0.82 "
0.5 "	0.81 "	0.82 "
0.6 "	0.82 "	0.83 "
0.7 "	0.86 "	0.88 "
0.8 "	0.89 "	0.92 "
1.0 "	0.95 "	0.99 "
1.1. "	0.97 "	1.01 "
1.2 "	0.99 "	1.04 "
1.3 "	1.02 "	1.07 "
1.4 "	1.05 "	1.11 "
1.5 "	1.10 "	1.17 "

(Vide curve No. 158)

i) 25 c.c. 0.009 M $CrCl_2$

= 1.55 c.c. 0.2 M K_4FeCy_6

= 12.2 c.c. 0.009 M

ii) 25 c.c. 0.009 $CrCl_2$

= 1.05 c.c. 0.2 M K_4FeCy_6

= 23.3 c.c. 0.009 M K_4FeCy_6

TABLE CLXXIX

Vol. of 0.454 M $CrCl_2$ = 1.0 c.c.

Vol. of alcohol = 0.0 c.c.

Total volume = 25 c.c.

∴ Conc. of $CrCl_2$ = 0.0182 M

Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	1.64×10^{-2}	1.64×10^{-2}
0.3 "	1.60 "	1.62 "
0.5 "	1.56 "	1.59 "
0.8 "	1.52 "	1.57 "
1.0 "	1.59 "	1.59 "
1.1 "	1.55 "	1.62 "
1.2 "	1157 "	1.65 "
1.5 "	1.63 "	1.72 "
1.8 "	1.69 "	1.80 "
2.0 "	1.68 "	1.81 "
2.2 "	1.61 "	1.75 "
2.3 "	1.60 "	1.75 "
2.5 "	1.64 "	1.80 "
3.0 "	1.85 "	2.07 "

(Vide curve No. 159)

i) 25 c.c. 0.018 M $CrCl_2$

= 0.95 c.c. 0.2 M K_4FeCy_6

= 10.6 c.c. 0.018 M K_4FeCy_6

ii) 25.0 c.c. 0.018 M $CrCl_2$

= 2.20 c.c. 0.2 M K_4FeCy_6

= 25.0 c.c. 0.018 M K_4FeCy_6

TABLE CLXXX

Vol. of 0.454 M $CrCl_2$ = 1.0 c.c.

Vol. of alcohol = 5.0 c.c.

Total volume = 25 c.c.

∴ Conc. of $CrCl_2$ = 0.0182 M

Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	1.44×10^{-2}	1.44×10^{-2}
0.3 "	1.44 "	1.46 "
0.5 "	1.44 "	1.47 "
0.8 "	1.43 "	1.48 "
1.0 "	1.44 "	1.50 "
1.1 "	1.44 "	1.50 "
1.2 "	1.45 "	1.52 "
1.5 "	1.48 "	1.57 "
1.8 "	1.52 "	1.63 "
2.0 "	1.54 "	1.66 "
2.2 "	1.52 "	1.65 "
2.3 "	1.53 "	1.67 "
2.5 "	1.58 "	1.74 "
3.0 "	1.7 "	1.90 "

(Vide curve No. 160)

i) 25 c.c. 0.018 M $CrCl_2$

= 1.03 c.c. 0.2 M K_4FeCy_6

= 11.44 c.c. 0.018 M K_4FeCy_6

ii) 25.0 c.c. 0.018 M $CrCl_2$

= 2.1 c.c. 0.2 M K_4FeCy_6

= 23.3 c.c. 0.018 M K_4FeCy_6

TABLE CLXXXI

Volume of 0.454 M $CrCl_2$ = 2.0 c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25 c.c.
∴ Conc. of $CrCl_2$ = 0.0363
Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	2.44 x 10^{-2}	2.44 x 10^{-2}
0.5 "	2.36 "	2.41 "
1.0 "	2.28 "	2.37 "
1.5 "	2.23 "	2.36 "
2.0 "	2.20 "	2.38 "
2.2 "	2.23 "	2.43 "
2.4 "	2.25 "	2.47 "
2.6 "	2.29 "	2.53 "
3.0 "	2.36 "	2.64 "
3.5 "	2.48 "	2.83 "
4.0 "	2.50 "	2.89 "
4.3 "	2.45 "	2.87 "
4.5 "	2.43 "	2.87 "
4.7 "	2.43 "	2.89 "
5.0 "	2.49 "	2.99 "
5.5 "	2.60 "	3.17 "

(Vide curve No. 161)

i) 25 c.c. 0.0363 M $CrCl_2$
= 1.9 c.c. 0.2 M K_4FeCy_6
= 10.47 c.c. 0.0363 M K_4FeCy_6

ii) 25 c.c. 0.0363 M $CrCl_2$
= 4.5 c.c. 0.2 M K_4FeCy_6
= 24.9 c.c. 0.0363 M K_4FeCy_6

TABLE CLXXXII

Volume of 0.454 M $CrCl_2$ = 2.0 c.c.
Volume of alcohol = 5.0 c.c.
Total volume = 25 c.c.
∴ Conc. of $CrCl_2$ = 0.0363
Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	2.08 x 10^{-2}	2.08 x 10^{-2}
0.5 "	2.07 "	2.11 "
1.0 "	2.07 "	2.15 "
1.5 "	2.1 "	2.23 "
2.0 "	2.12 "	2.29 "
2.2. "	2.14 "	2.33 "
2.4 "	2.16 "	2.37 "
2.6 "	2.19 "	2.42 "
3.0 "	2.25 "	2.52 "
3.3 "	2.31 "	2.63 "
4.0 "	2.35 "	2.73 "
4.3 "	2.34 "	2.74 "
4.5 "	2.34 "	2.76 "
4.7 "	2.34 "	2.78 "
5.0 "	2.36 "	2.83 "
5.5 "	2.42 "	2.95 "

(Vide curve No. 162)

i) 25 c.c. 0.0363 M $CrCl_2$
= 2.0 c.c. 0.2 M K_4FeCy_6
= 11.03 c.c. 0.0363 M K_4FeCy_6

ii) 25 c.c. 0.0363 M $CrCl_2$
= 4.5 c.c. 0.2 M K_4FeCy_6
= 24.8 c.c. 0.0363 M K_4FeCy_6

CONDUCTOMETRIC TITRATIONS BETWEEN [illegible]

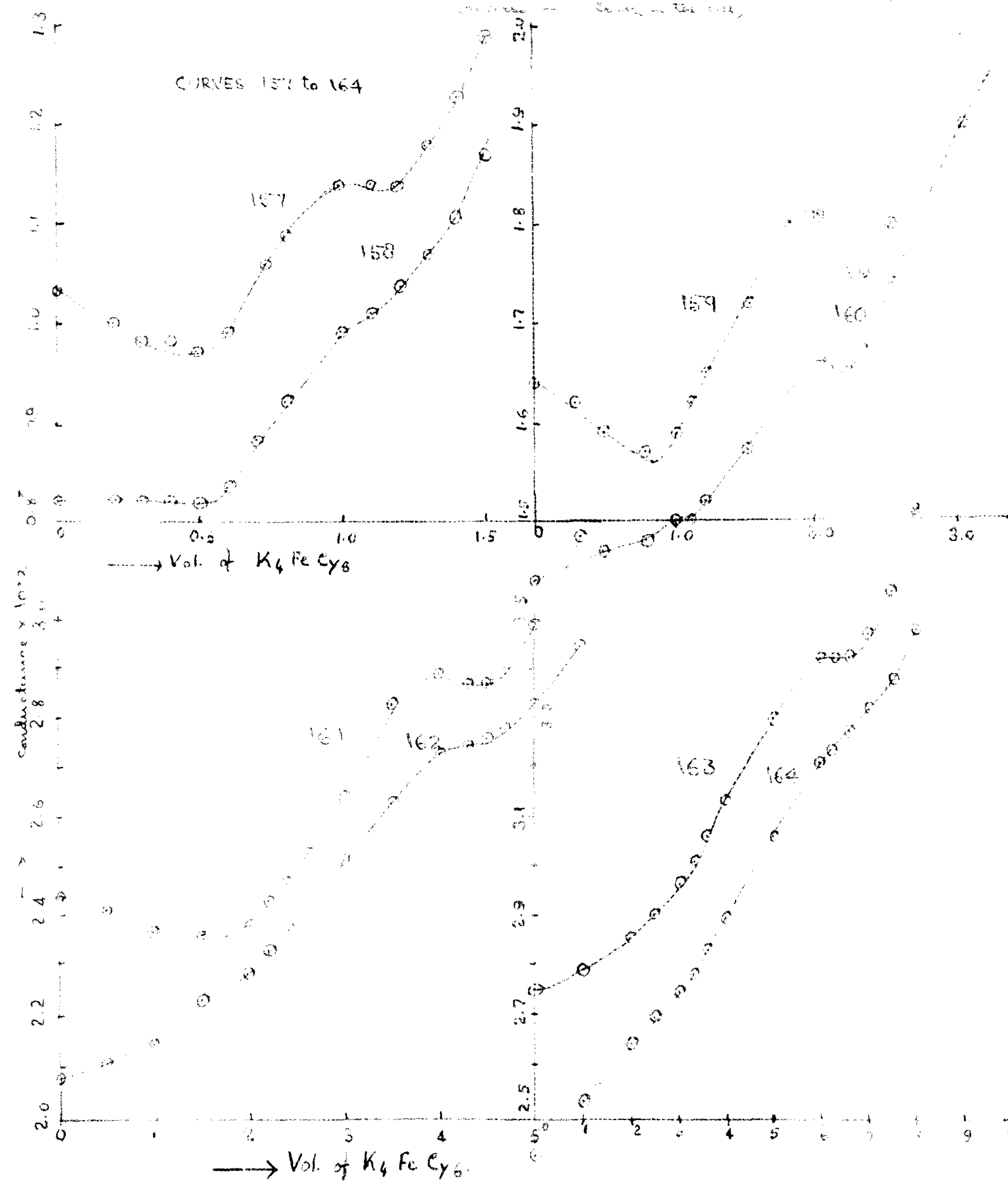


TABLE CLXXXIII

Volume of 0.454 M $CrCl_2$ = 3.0 c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25 c.c.
∴ Conc. of $CrCl_2$ = 0.0545
Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	2.75×10^{-2}	2.75×10^{-2}
1.0 "	2.68 "	2.79 "
2.0 "	2.64 "	2.85 "
2.5 "	2.64 "	2.90 "
3.0 "	2.65 "	2.97 "
3.3. "	2.66 "	3.01 "
3.6 "	2.67 "	3.06 "
4.0 "	2.70 "	3.13 "
5.0 "	2.75 "	3.30 "
6.0 "	2.76 "	3.42 "
6.3 "	2.73 "	3.42 "
6.6 "	2.70 "	3.42 "
700 "	2.71 "	3.47 "
7.5 "	2.74 "	3.56 "
8.0 "	2.82 "	3.72 "

(vide curve No. 163)

i) 25 c.c. .05454 M $CrCl_2$
= 3.0 c.c. 0.2 M K_4FeCy_6
= 11.01 c.c. 0.0545 M K_4FeCy_6

ii) 25 c.c. .0545 M $CrCl_2$
= 6.7 c.c. 0.2 M K_4FeCy_6
= 24.6 c.c. 0.0545 M K_4FeCy_6

TABLE CLXXXIV

Volume of 0.454 M $CrCl_2$ = 3.0 c.c.
Volume of alcohol = 5.0 c.c.
Total volume = 25 c.c.
∴ Conc. of $CrCl_2$ = 0.0545
Strength of K_4FeCy_6 = 0.2 M

Vol. of K_4FeCy_6	Conductance	Corrected conductance
0.0 c.c.	2.43×10^{-2}	2.43×10^{-2}
1.0 "	2.43 "	2.53 "
2.0 "	2.44 "	2.64 "
2.5 "	2.45 "	2.70 "
3.0 "	2.46 "	2.75 "
3.3 "	2.46 "	2.75 "
3.6 "	2.47 "	2.83 "
4.0 "	2.49 "	2.89 "
5.0 "	2.55 "	3.06 "
6.0 "	2.59 "	3.21 "
6.3 "	2.59 "	3.24 "
6.6. "	2.59 "	3.27 "
7.0 "	2.59 "	3.32 "
7.5 "	2.60 "	3.38 "
8.0 "	2.63 "	3.47 "

(vide curve No. 164)

i) 25 c.c. 0.0545 M $CrCl_2$
= 3.4 c.c. 0.2 M K_4FeCy_6
= 12.47 c.c. 0.0545 M K_4FeCy_6

ii) 25 c.c. 0.0545 M $CrCl_2$
= 6.5 c.c. 0.2 M K_4FeCy_6
= 23.85 c.c. 0.0545 M K_4FeCy_6

TABLE CLXXXV.

Summarised table on the Direct Titrations

(K_4FeCy_6 in the cell)

Conc. of K_4FeCy_6	Percentage of alcohol	Vol. of K_4FeCy_6	Conc.of $CrCl_2$	Vol.of $CrCl_2$ equivalent to 25 c.c. K_4FeCy_6	Probable Ratio	Remarks.
0.01 M	0.0	25 c.c.	0.454 M	i)22.7 c.c. ii)47.67 c.c.	1:1 1:2	Both the breaks are sharpthough the first more prominent.
0.01 M	8.0 %	25 c.c.	0.454 M	i)24.06 c.c. ii)47.12 c.c.	1:1 1:2	Second break less prominent.
0.01 M	20.0 %	25 c.c.	0.454 M	i)24.97 c.c. ii)49.03 c.c.	1:1 1:2	The second break not very sharp.
0.02 M	0.0	25 c.c.	0.454 M	i)23.38 c.c. ii)47.67 c.c.	1:1 1:2	Two distinct breaks are obtained in all the three cases.
0.02 M	8.0 %	25 c.c.	0.454 M	i)24.06 c.c. ii)46.76 c.c.	1:1 1:2	but the second breaks are not as
0.02 M	20.0 %	25 c.c.	0.454 M	i)24.97 c.c. ii)43.1 c.c.	1:1 1:2	sharp as the first.
0.03 M	0.0 %	25 c.c.	0.454 M	i)22.5 c.c ii)47.56 c.c.	1:1 1:2	There is very little inflection at the second point.
0.03 M	8.0 %	25 c.c.	0.454 M	i)24.16 c.c. ii)46.8 c.c.	1:1 1:2	Second inflection still smaller than in the previous case
0.03 M	20.0 %	25 c.c.	0.454 M	i)24.6 c.c.	1:1	No second break.
0.05 M	0.0	25 c.c.	0.454 M	ii)23.61 c.c. ii)43.6 c.c.	1:2 1:2	Second break appear in two
0.05 M	8.0 %	25 c.c.	0.454 M	i)24.06 c.c. ii)48.1 c.c.	1:1 1:2	cases(with o % & 8 % alcohol) but not as sharp as
0.05 M	20.0 %	25 c.c.	0.454 M	1)24.97 c.c.	1:1	the first. Equivalenceepoint could very well be located. No inflection with 20% alcohol.

TABLE CLXXXVI.

Summarised table on the reverse titrations

($CrCl_2$ in the cell)

Conc.of $CrCl_2$ 633	Percentage of alcohol	Vol.of $CrCl_2$	Conc.of K_4FeCy_6	Vol.of K_4FeCy_6 equivalent to 25 c.c. $CrCl_2$	Probable ratio	Remarks
0.0091 M	0.0	25 c.c.	0.2 M	i)11.3 c.c. ii)25.1 c.c.	1:2 1:1	Both the breaks sharp
0.0091 M	20.0 %	25 c.c.	0.2 M	i)12.2 c.c. ii)23.3 c.c.	1:2 1:1	Second inflection not as sharp as the first.
0.0182 M	0.0	25 c.c.	0.2 M	i)10.6 c.c. ii)25.0 c.c.	1:2 1:1	Both the breaks sharp.
0.0182 M	20.0%	25 c.c.	0.2 M	i)11.44 c.c. ii)23.3 c.c.	1:2 1:1	Both the breaks sharp.
0.0363 M	0.0	25 c.c.	0.2 M	i)10.47 ccc. ii)24.8 c.c.	1:2 1:1	Both the breaks sharp.
0.03636M	20.0 %	25 c.c.	0.2 M	i)11.03 c.c. ii)24.8 c.c.	1:2 1:1	First break not as distinct as the second.
0.0544 M	0.0	25 c.c.	0.2 M	i)11.01 c.c. ii)24.6 c.c.	1:2 1:1	First break not very prominent.
0.05444M	20.0 %	25 c.c.	0.2 M	i)12.47 c.c. ii)23.85 c.c.	1:2 1:2	Verysmall inflection at the first point.

Discussion:

An analysis of the curves and results on the conductometric titrations (both direct and reverse and those in aquous and non-aquous media) between chromous chloride and potassium ferrocyanide provide intresting and useful information of the complex. Although both the direct and the reverse titrations point towards the formation of two compounds at different stages of mixing the reagents the second break is not very distinct and in some cases not even traceable (vide curves 145 to 156) in the case of direct titration(potassium ferrocyanide in the cell), this behaviour persists in the reverse titrations also(chromous chloride in the cell) but the number of cases in which the first break (just the opposite for the direct titration) is less distinct are small when compared with the curves for direct titrations (vide curves 157 - 164). In all cases the shape of the curve is very much influenced by the addition of alcohol. The conductance values are very low in the begining, as it should be, but rise to a maximum and then fall to give T shaped titration curves, just similar to those as in the aquous medium.

The probable reactions between chromous chloride and potassium ferrocyanide may be represented as:

1. $CrCl_2 + K_4FeCy_6 = K_2Cr_2FeCy_6 + 2KCl$
2. $2CrCl_2 + K_4FeCy_6 = Cr_2FeCy_6 + 4KCl$
3. $3CrCl_2 + K_4FeCy_6 = K_2Cr_3(FeCy_6)_2 + 6KCl$

For the direct titrations the volume of chromous chloride required for the completion of the reaction in aquous medium is

below the theoritical value (22.7 c.c. of $CrCl_2$ for 25 c.c. of K_4FeCy_6) as required by reaction(1). It may, however, be seen that the titre value approaches the theoritical value when titrations are carried out in aqueous-alcoholic medium (24.97 c.c. in 20 % alcohol vide summarised table). The behaviour was observed for all the four concentrations. These observations show the existance of a complex of composition $K_2CrFeCy_6$ in the freshly precipitated state when chromous chloride is added to potassium ferrocyanide. The increase in the titre value in presence of alcohol maybe due to the suppression of adsorption. It is quite likely that the complex formed adsorbs some of the $FeCy_6^{-4}$ thereby using up some of the ferrocyanide solution. This tendency is checked in presence of alcohol with the result that the theoritical value as necessary for the formation of $K_2CrFeCy_6$ is reached.

The second breaks in the direct titrations in majority of cases are not sharp but whatever little information could be obtained from these values, the possibility of the existance of a compound having the composition Cr_2FeCy_6 can be seen. Addition of alcohol does bring about an increase in the titre values in some cases, but the behaviour is not uniform (vide curve Nos.145-156).

Considering the reverse titrationss it will be found that the first break is not as prominent (vide curve Nos.157-164) as the second break. The results point towards the formation of Cr_2FeCy_6 the value approaching the theoritical value in presence of alcohol (12.67 c.c., 12.44, 12.47 c.c. in 20 % alcohol for $CrCl_2$ of conc. .0001 M, .0[illegible] M and 0.0544 M respectively). In no case the value reach the theoritical value 12.5 c.c. for the [illegible] $CrCl_2$

as 1:2. The discrepancy in the values for the aquous and aquous-alcoholic media can be explained again on the basis of the adsorption of $FeCy_6$. The values for the second break, in the case of reverse titrations, give the ratio of mixing of K_4FeCy_6:$CrCl_2$ as 1:1 (that is, the formation of $K_2CrFeCy_6$) in the aquous medium. The effect of alcohol on the titre value for the second break is, however, different than for other case, the titre value showing a decrease in presence of alcohol. It may be due to the suppression of hydrolysis by the freshly precipitated complex. On hydrolysis the precipitate might release Cr^{++} ion which need a larger amount of ferrocyanide than when the tendency is shecked by the presence of alcohol.

(c). Potentiometric Titrations between $CrCl_2$ and $K_4Fe(CN)_6$.

Potentiometric titrations have been employed by a number of workers (Lenden, Calvin and Melchior, Ray and co-worker, Tradwell and Huber)[24-27] to demonstrate complex formation as well as to determine the formulae of such compounds. In recent years Bhattacharya and co-workers (loc. cit) have applied this method to determine the composition of some ferrocyanogen complexes. With a view to confirm the results arrived at for the chromous ferrocyanide complex attempt was made to apply potentiometric titrations for ascertaining the composition for this insoluble complex. This may also incidentally provide a method for the estimation of Cr(ii) by titrating against K_4FeCy_6.

A potentiometric titration is one in which the end point is detected by measuring the change in potential of suitable indicator electrode during the titration. The determining factor in the potential of an indicator electrode is the ratio of the activities (or effective concentrations) of the oxidised and reduced forms of the ion. The fundamental equation connecting the chemical equilibria and electrochemical measurements, is given as:

$$E = E_0 - \frac{RT}{nF} \log \frac{\text{oxidised state}}{\text{reduced state}}$$

where E is the potential for the mixture of the oxidised and reduced form of the active ion and E_0 , its standard electrode potential (when the ratio = 1).

In order to use this equation quantitavely, it is necessary to have reversible electrode, but the end point in a titration curve can be determined empirically without the use of this theoretical equation and even with electrodes that are not necessarily reversible.

Under these conditions the end point is determined by the rapid change in potential when a small amount of the reagent is added. The steepest part ofthe curve, when the voltage is plotted vertically against the number of millilitores of reagent added, indicates the point at which the two reactants are present in chemically equivalent amounts.

Platinum is the most important and extensively used indicator electrode in measuring the redox potential change for oxidation reduction titrations and also in the estimation of metal ions. Amongst the extensively used reagent is the mixture of potassium ferro and ferricyanide which has been successively used for the estimation of zinc[20,21] and to some extent to the estimation of cadmium[21] , lead, copper etc.[20] For certain metals, however, the method could not be applied because in some cases peculiar curves were obtained while in others sharp fall in potential could not be observed(e.g. silver).

Both direct and reverse titrations between chromous chloride and potassium ferrocyanide were tried using platinum indicator electrode and a saturated calomel reference electrode. Since no sharp breaks were obtained in reverse titration. Direct titrations (ferrocyanide in the cell) only were carried out both in the aqueous and the aqueous alcoholic media.

EXPERIMENTAL.

a. Reagents:

Chromous chloride and potassium ferrocyanide solution required for these potentiometric titrations were prepared and standardised earlier.

b. Apparatus:

A Varnier potentiometer (Type 3387B) in conjunction with a

[illegible] coil galvonometer with lamp and scale out fit was used for the experiments. The air tight titration cell (described on page 24) with a smooth platinum wire electrode and a saturated calomel electrode served quite satisfactorily. Purified nitrogen was used for deaeration and continuous current of the gas served as an effective stirrer.

c. Prodedure of the experiments:

A known volume of the standard potassium ferrocyanide was diluted to a constant volume of 25 c.c. with double distilled water in the titration cell and a continuous current of nitrogen was passed through it for complete deaeration of the solution and to replace all the air in the cell. About half an hour after aliquots of chromous chloride were added from the microburette and the potentials noted down five minutes after each addition (this time was sufficient for the attainment of the equilibrium and to give a constant value). The current of nitrogen was cut off for a while at the time of taking the readings. The potential was then plotted against the volume of chromous chloride added and the equivalence point determined from steepness of inflection of the curve. Titrations were carried out with different concentrations of the reagents and also in presence of alcohol.

TABLE CLXXXVII.

Volume of 0.1 M K_4FeCy_6 = 2.5 c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25.0c.c.
∴Strength of K_4FeCy_6 = 0.01 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of CrCl	Pt. vs s.c.e.
0.0 c.c.	0.061
0.1 c.c.	-0.024
0.2 c.c.	-0.0305
0.3 c.c.	-0.028
0.4 c.c.	-0.026
0.5 c.c.	-0.0505
0.6 c.c.	-0.058
0.7 c.c.	-0.0575
0.8 c.c.	-0.055
0.9 c.c.	-0.055
1.0 c.c.	-0.0585
1.1 c.c.	-0.0850
1.2 c.c.	-0.090
1.5 c.c.	-0.096

(Vide curve No. 165)

i)25 c.c. 0.01 M K_4FeCy_6
= 0.5 c.c. of 0.454 M $CrCl_2$
= 22.7cc0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6
= 1.08 c.c. 0.454 M $CrCl_2$
= 49.03 c.c. 0.01 M $CrCl_2$

TABLE CLXXXVIII.

Volume of 0.1 M K_4FeCy_6 = 2.5.c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25.0c.c.
∴Strength of K_4FeCy_6 = 0.01 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of CrCl	Pt. vs. s.c.e
0.0 c.c.	0.035
0.1 c.c.	-0.012
0.2 c.c.	-0.145
0.3 c.c.	-0.0155
0.5 c.c.	-0.018
0.6 c.c.	-0.039
0.7 c.c.	-0.042
0.8 c.c.	-0.044
1.0 c.c.	-0.0465
1.1.c.c.	-0.068
1.2 c.c.	-0.076
1.3 c.c.	-0.0795
1.4 c.c.	-0.081
1.5 c.c.	-0.083

(Vide curve No. 166)

i) 25 c.c. 0.01 M K_4FeCy_6
= o.55 c.c. $CrCl_2$
= 24.97 c.c. 0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6
= 1.08 c.c. 0.454 M $CrCl_2$
= 49.03 c.c. 0.01 M $CrCl_2$

TABLE CLXXXIX

Volume of 0.1 M K_4FeCy_6 = 2.5 c.c.
Volume of alcohol = 5.0 c.c.
Total volume = 25.0 c.c.
∴ Strength of K_4FeCy_6 = 0.01 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.026
0.1 "	-0.011
0.2 "	-0.013
0.4 "	-0.0165
0.5 "	-0.020
0.6 "	-0.038
0.8 "	-0.044
0.9 "	-0.047
1.0 "	-0.050
1.1. "	-0.0665
1.2 "	-0.077
1.3 "	-0.0805
1.4 "	-0.083
1.5 "	-0.085

(Vide curve No. 167)

i) 25 c.c. 0.01 M K_4FeCy_6
= 0.56 c.c. 0.454 M $CrCl_2$
= 25.42 c.c. 0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6
= 1.1 c.c. 0.454 M $CrCl_2$
= 49.94 c.c. 0.01 M $CrCl_2$

TABLE CLXC

Volume of 0.1 M K_4FeCy_6 = 5.0 c.c.
Volume of alcohol = 0.0 c.c.
Total volume = 25 c.c.
∴ Strength of K_4FeCy_6 = 0.02 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.011
0.2 "	-0.0375
0.3 "	-0.040
0.5 "	-0.037
0.7 "	-0.033
0.9 "	-0.0375
1.0 "	-0.075
1.2 "	-0.082
1.4 "	-0.079
1.6 "	-0.073
1.8 "	-0.0705
2.0 "	-0.076
2.1 "	-0.109
2.3 "	-0.119
2.5 "	-0.1112

(Vide curve No. 168)

i) 25 c.c. 0.02 M K_4FeCy_6
= 1.0 c.c. 0.454 M $CrCl_2$
= 23.15 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 2.1 M 0.454 M $CrCl_2$
= 47.67 c.c. 0.02 M $CrCl_2$

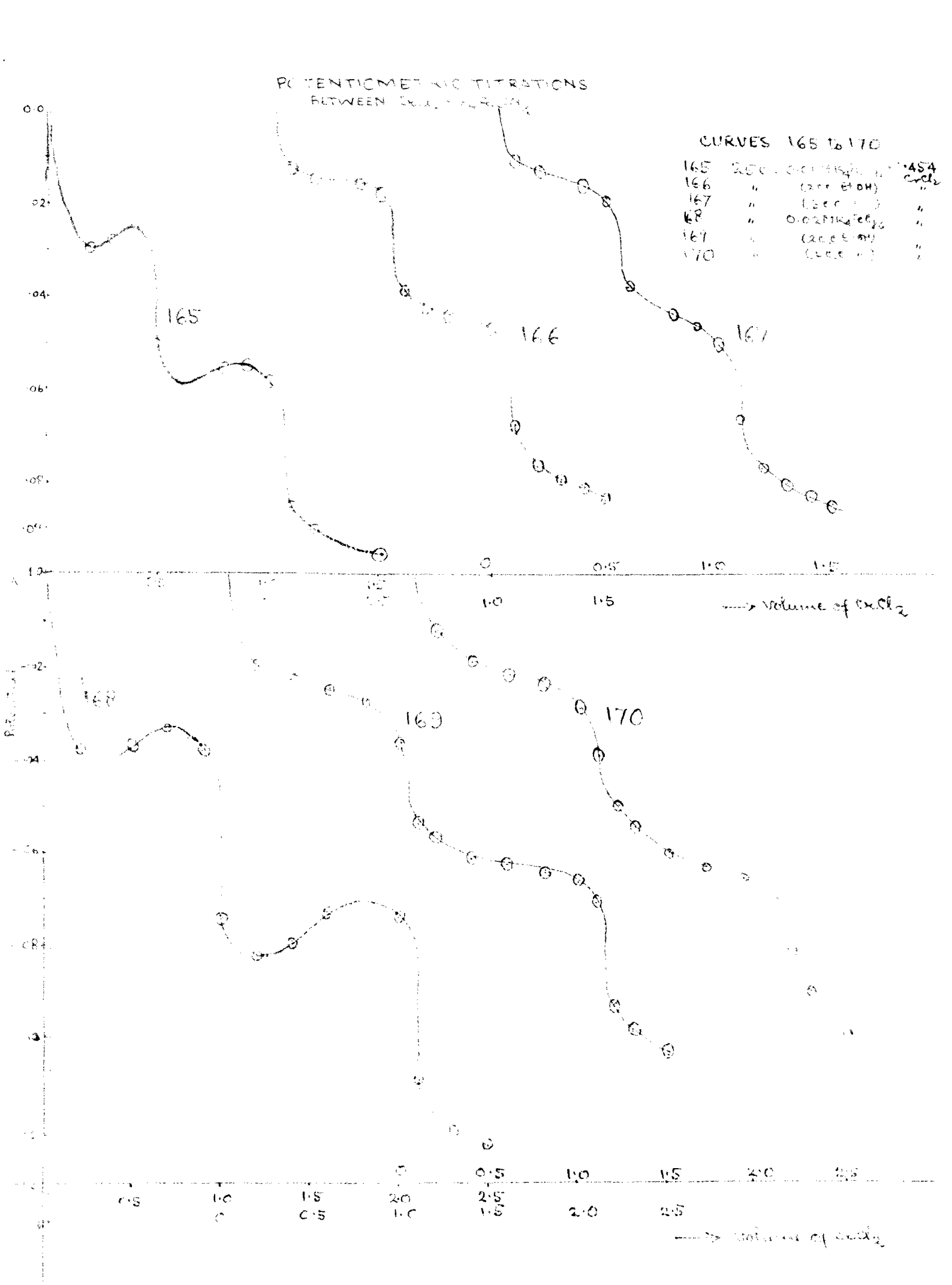

POTENTIOMETRIC TITRATIONS
CURVES 165 to 170
165
166
167
168
169
170
0·0
0·2
0·4
0·6
0·8
1·0
0·5
1·0
1·5
2·0
2·5
Volume of

TABLE CLXCI

Volume of 0.1 M K_4FeCy_6 = 5.0 c.c.
Volume of alcohol = 2.0 c.c.
Total volume made up = 25 c.c.
∴ Strength of K_4FeCy_6 = 0.02 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.014
0.2 "	-0.020
0.4 "	-0.0225
0.6 "	-0.0245
0.8 "	-0.027
1.0 "	-0.036
1.1 "	-0.053
1.2 "	-0.056
1.4 "	-0.061
1.6 "	-0.062
1.8 "	-0.065
2.0 "	-0.066
2.1 "	-0.071
2.2 "	-0.093
2.3 "	-0.0985
2.5 "	-0.103

(Vide curve No. 169)

i) 25 c.c. 0.02 M K_4FeCy_6
= 1.05 c.c. 0.454 M $CrCl_2$
= 23.83 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 2.15 c.c. 0.454 M $CrCl_2$
= 48.8 c.c. 0.02 M $CrCl_2$

TABLE CLXCII

Volume of 0.1 M K_4FeCy_6 = 5.0 c.c.
Volume of alcohol = 5.0 c.c.
Total volume made up = 25 c.c.
∴ Strength of K_4FeCy_5 = 0.02 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.021
0.2 "	-0.012
0.4 "	-0.018
0.6 "	-0.021
0.8 "	-0.0235
1.0 "	-0.028
1.1 "	-0.039
1.2 "	-0.050
1.3 "	-0.054
1.5 "	-0.0595
1.7 "	-0.063
1.9 "	-0.065
2.1 "	-0.070
2.2 "	-0.082
2.3 "	-0.0915
2.5 "	-0.100

(Vide curve No. 170)

i) 25 c.c. 0.02 M K_4FeCy_6
= 1.08 c.c. $CrCl_2$
= 24.51 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 2.18 c.c. 0.454 M $CrCl_2$
= 49.49 c.c. 0.02 M $CrCl_2$

TABLE CLXCIII

Volume of 0.1 M K_4FeCy_6 = 10.0 c.c.
Volume of alcohol = 0.0 c.c.
Total volume made up = 25.0 c.c.
∴ Strength of K_4FeCy_6 = 0.04 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.035
0.2 "	-0.017
0.4 "	-0.0355
0.8 "	-0.041
1.0 "	-0.040
1.3 "	-0.038
1.5 "	-0.038
1.8 "	-0.0415
2.0 "	-0.069
2.3 "	-0.079
2.6 "	-0.080
3.0 "	-0.079
3.3 "	-0.077
3.7 "	-0.079
4.0 "	-0.085
4.2 "	-0.115
4.5 "	-0.121
5.0 "	-0.126

(Vide curve No. 171)

i) 25 c.c. 0.04 M K_4FeCy_6
= 2.0 c.c. $CrCl_2$
= 22.7 c.c. 0.04 M $CrCl_2$

ii) 25 c.c. 0.04 M K_4FeCy_6
= 4.1 c.c. 0.454 M $CrCl_2$
= 46.54 c.c. 0.04 M $CrCl_2$

TABLE CLXCIV

Volume of 0.1 M K_4FeCy_6 = 10.0 c.c.
Volume of alcohol = 2.0 c.c.
Total volume made up = 25 c.c.
∴ Strength of K_4FeCy_6 = 0.04 M
Conc. of $CrCl_2$ = 0.454 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.058
0.3 "	-0.008
0.55 "	-0.0125
1.0 "	-0.014
1.3 "	-0.015
1.6 "	-0.016
2.0 "	-0.030
2.2. "	-0.043
2.5 "	-0.0475
2.8 "	-0.049
3.2 "	-0.050
3.5 "	-0.0525
3.8 "	-0.057
4.0 "	-0.064
4.2 "	-0.0845
4.5 "	-0.094
5.0 "	-0.099

(Vide curve No. 172)

i) 25 c.c. 0.04 M K_4FeCy_6
= 2.05 c.c. 0.454 M $CrCl_2$
= 2.05 c.c. 0.454 M $CrCl_2$

ii) 25 c.c. 0.04 M K_4FeCy_6
= 4.15 c.c. 0454 M $CrCl_2$
= 4715 c.c. 0.04 M $CrCl_2$

TABLE CLXCV

Volume of 0.1 M K_4FeCy_6 = 10 c.c.
Volume of alcohol = 5.0 c.c.
∴ Strength of K_4FeCy_6 = 0.04 M
Conc. of $CrCl_2$ = 0.236 M
Total volume made up = 25 c.c.

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.051
0.3 "	-0.0045
0.6 "	-0.010
1.0 "	-0.015
1.3 "	-0.017
1.6 "	-0.019
2.0 "	-0.028
2.2 "	-0.0365
2.4 "	-0.040
2.7 "	-0.0435
3.0 "	-0.046
3.5 "	-0.051
4.0 "	-0.059
4.2 "	-0.0655
4.4 "	-0.076
4.6 "	-0.082
5.0 "	-0.089

(Vide curve No. 173)

i) 25 c.c. 0.04 M K_4FeCy_6
= 2.15 c.c. 0.454 M $CrCl_2$
= 24.4 c.c. 0.04 M $CrCl_2$

ii) 25 c.c. 0.04 M K_4FeCy_6
= 4.3 c.c. 0454 M $CrCl_2$
= 48.75 c.c. 0.04 M $CrCl_2$

TABLE CLXCVI

Volume of 0.1 M K_4FeCy_6 = 5.0 c.c.
Total volume made up = 25 c.c.
∴ Strength of K_4FeCy_6 = 0.02 M
Conc. of $CrCl_2$ = 0.236 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.0456
0.5 "	-0.011
0.8 "	-0.016
1.0 "	-0.0155
1.8 "	-0.0180
1.6 "	-0.010
2.0 "	-0.014
2.2 "	-0.036
2.4 "	-0.044
2.6 "	-0.0465
3.0 "	-0.046
3.3 "	-0.043
3.6 "	-0.043
4.0 "	-0.0466
4.2 "	-0.067
4.4 "	-0.086
4.6 "	-0.095

(Vide curve No. 174)

i) 25 c.c. 0.02 M K_4FeCy_6
= 2.2 c.c. 0.236 M $CrCl_2$
= 23.6 c.c. 0.02 M $CrCl_2$

ii) 25 c.c. 0.02 M K_4FeCy_6
= 4.3 c.c. 0.236 M $CrCl_2$
= 50.74 c.c. 0.02 M $CrCl_2$

POTENTIOMETRIC TITRATIONS BETWEEN [illegible]

CURVES 171 to 176

171 0.04M K_4Fecy_6 x 0.454M $Cucl_2$

172 " " " x "

173 " " (5cc ") x "

174 0.01M K_4Fecy_6 x 0.236M $Cucl_2$

175 0.02M K_4Fecy_6 x " "

176 0.01M K_4Fecy_6 x 0.108M $Mucl_2$

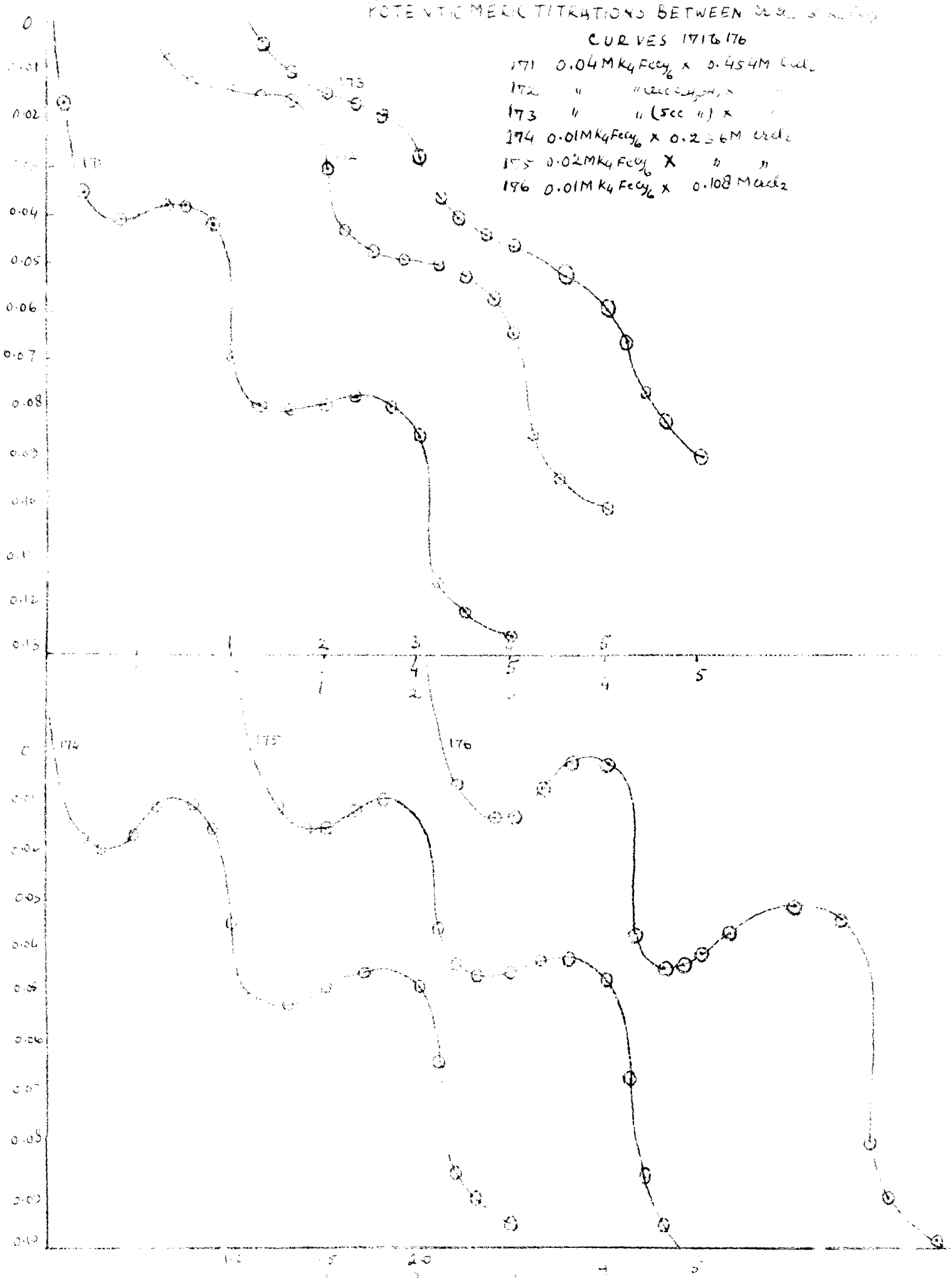


TABLE CLXCVII

Volume of 0.1 M K_4FeCy_6 = 2.5 c.c.

Total volume made up = 25 c.c.

∴ Strength of K_4FeCy_6 = 0.01 M

Conc. of $CrCl_2$ = 0.236 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.032
0.2 "	-0.018
0.3 "	-0.020
0.5 "	-0.0165
0.6 "	-0.011
0.8 "	-0.011
0.9 "	-0.0155
1.0 "	-0.0355
1.1 "	-0.050
1.3 "	-0.052
1.5 "	-0.048
1.7 "	-0.045
2.0 "	-0.048
2.1 "	-0.063
2.2 "	-0.085
2.3 "	-0.088
2.5 "	-0.096

(Vide curve No. 175)

i) 25 c.c. 0.01 M K_4FeCy_6

= 1.0 c.c. 0.236 $CrCl_2$

= 23.6 c.c. 0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6

= 2.15 c.c. 0.236 M $CrCl_2$

= 50.64 c.c. 0.01 M $CrCl_2$

TABLE CLXCVIII

Volume of 0.1 M K_4FeCy_6 = 2.5 c.c.

Total volume made up = 25 c.c.

∴ Strength of K_4FeCy_6 = 0.01 M

Conc. of $CrCl_2$ = 0.108 M

Vol. of $CrCl_2$	Pot. vs. s.c.e.
0.0 c.c.	0.032
0.4 "	-0.006
0.8 "	-0.013
1.0 "	-0.013
1.3 "	-0.007
1.6 "	-0.002
2.0 "	-0.002
2.3 "	-0.037
2.6 "	-0.044
2.8 "	-0.044
3.0 "	-0.042
3.3 "	-0.037
4.0 "	-0.032
4.5 "	-0.034
4.8 "	-0.079
5.0 "	-0.090
5.5 "	-0.099

(Vide curve No. 176)

i) 25 c.c. 0.01 M K_4FeCy_6

= 2.3 c.c. 0.0108 M $CrCl_2$

= 24.84 c.c. 0.01 M $CrCl_2$

ii) 25 c.c. 0.01 M K_4FeCy_6

= 4.8 c.c. 0.108 M $CrCl_2$

= 50.26 c.c. 0.01 M $CrCl_2$

TABLE CLXCIX

Summarised table for potentiometric titrations

Curve No.	Conc.of K_4FeCy_6	Percentage of alcohol	Conc.of $CrCl_2$	Vol.of .454 $CrCl_2$	Vol.of $CrCl_2$ equivalent to K_4FeCy_6	Probable ratio K_4FeCy_6 : $CrCl_2$
165	0.01 M	0.0	0.454M	i) 0.5 c.c.	22.7 c.c.	1:1
				ii) 1.08c.c.	49.03 c.c.	1:2
166	0.01 M	8.0	0.454M	i) 0.55 c.c.	24.97 c.c.	1:1
				ii) 1.08 c.c.	49.03 c.c.	1:2
167	0.01 M	20.0	0.454M	i) 0.56 c.c.	25.42 c.c.	1:1
				ii) 1.1 c.c.	49.94 c.c.	1:2
168	0.02 M	0.0	0.454M	i) 1.0 c.c.	23.15 c.c.	1:1
				ii) 2.1 c.c.	47.67 c.c.	1:2
169	0.02 M	8.0	0.454M	i) 1.05 c.c.	23.83 c.c.	1:2
				ii) 2.15 c.c.	48.8 c.c.	1:1
170	0.02 M	20.0	0.454M	i) 1.08 c.c.	24.51 c.c.	1:1
				ii) 2.18 c.c.	49.49 c.c.	1:2
171	0.04 M	0.0	0.454M	i) 2.0 c.c.	22.7 c.c.	1:1
				ii) 4.1 c.c.	46.54 c.c.	1:2
172	0.04 M	8.0	0.454M	i) 2.05 c.c.	23.29 c.c.	1:1
				ii) 4.15 c.c.	47.10 c.c.	1:2
173	0.04 M	20.0	0.454M	i) 2.15 c.c.	24.4 c.c.	1:1
				ii) 4.3 c.c.	48.[illegible] c.c.	1:2
174	0.02 M	0.0	0.236M	i) 2.2 c.c.	23.6 c.c.	1:1
				ii) 4.3 c.c.	48.75 c.c.	1:2
175	0.01 M	0.0	0.236M	i) 1.0 c.c.	23.6 c.c.	1:1
				ii) 2.15 c.c.	50.74 c.c.	1:2
176	0.01 M	0.0	0.108M	i) 2.3 c.c.	24.84 c.c.	1:1
				ii) 4.8 c.c.	50.26 c.c.	1:2

Discussion.

My results on the titre values for the potentiometric titrations between potassium ferrocyanide(in the cell) and chromous chloride, carried out at different concentrations and in aqueous and aqueous-alcoholic medium, give support to the earlier conclusions arrived at on the basis of conductometric studies. Evidence is available for the formation of the distinct complexes with definite co compositions. The molar ratios in which chromous chloride and potassium ferrocyanide react are 1:1 and 1:2, pointing towards the formation of $K_2CrFeCy_2$ and Cr_2FeCy_6 respectively.

A difference in the nature of the titration curve may be observed for those carried out in aqueous and aqueous-alcoholic medium. It will be seen from the curves (curve No. 165, 168, 171, 175 and 176) that a big rise in potential is observed near the equivalence point for the aqueous medium, the curves becoming more drawn out, and, consequently, less sharp in the aqueous-alcoholic medium (curves nos.

A perusal of column 6 of the summarised table for curves from 165 to 173 shows that the theoretical values of chromous chloride are more or less obtained for the breaks when titrations are carried out in presence of alcohol. In the absence of alcohol the values are too low (e.g. 22.7 c.c. from curve 165 for break I) and this can be explained assuming that the complex formed in excess of K_3FeCy_3 keeps a part of the latter in the adsorbed state making it unavailable for the reaction. Similar observations are obtained in the case of the second breaks also. Alcohol suppresses this adsorption and hence values near the theoretical, are obtained when titrations are carried out in aqueous-alcoholic media.

The dilution of the reactants seems to influence the successful application of these titrations to a great extent. It may be seen that on diluting chromous chloride from 0.454 M to 0.236 M, the volume of $CrCl_2$ required for 25 c.c. of 0.02 M K_4FeCy_6 rises from 23.15 c.c. to 23.6 c.c. Similarly with 0.01 M potassium ferrocyanide, the equivalent volumes are 22.7 c.c.; 23.6 c.c.; and 24.8 c.c. for concentrations of chromous chloride 0.454 M, 0.236 M and 0.108 M respectively. Such a uniformity in behaviour, however, is not observed when titre values for the second break are considered. It is thus evident that results approaching the theoretical values are also obtained when titrations are carried out with dilute solutions of both the reactants.

(d). Amperometric Titrations:

The technique of amperometric titration for the estimation of elements and ions, occupies an important place with other electrometric titration procedures such as potentiometry, coulometry and conductometry. The technique was first introduced in the analytical field by Sease, Niemann and Swift[22] in 1947. It is based on the establishment of conditions such as either the substance being determined or the titrant undergoes reaction at an indicator electrode[9] (usually a dropping mercury electrode or a rotating platinum micro-electrode) to produce a current which is proportional to the concentration of the indicator electrode held constant the end point can be established from the course of the current change during the titration. Hence it is a titration performed by adding successive aliquots of a standard solution of a reagent to a solution of the sample and measuring the diffusion current after each addition. Depending on the potential applied to the cell, the diffusion current may be proportional to the concentration of the substance or of the excess of the reagent, or of one of the products of reaction. The titration graph (current vs. volume of titrant) usually consists of two straight lines whose intersection is at (or very near) the equivalence point. The constant potential to be applied is always first determined from a polarogram of the titrant. Thus it is not essential to use a titrating reagent which reduces at the dropping mercury electrode, since the end point can still be located with a non-reducible reagent. Similarly an element(or radical) which does not produce a step can be determined by using a precipitating

FIG. 7

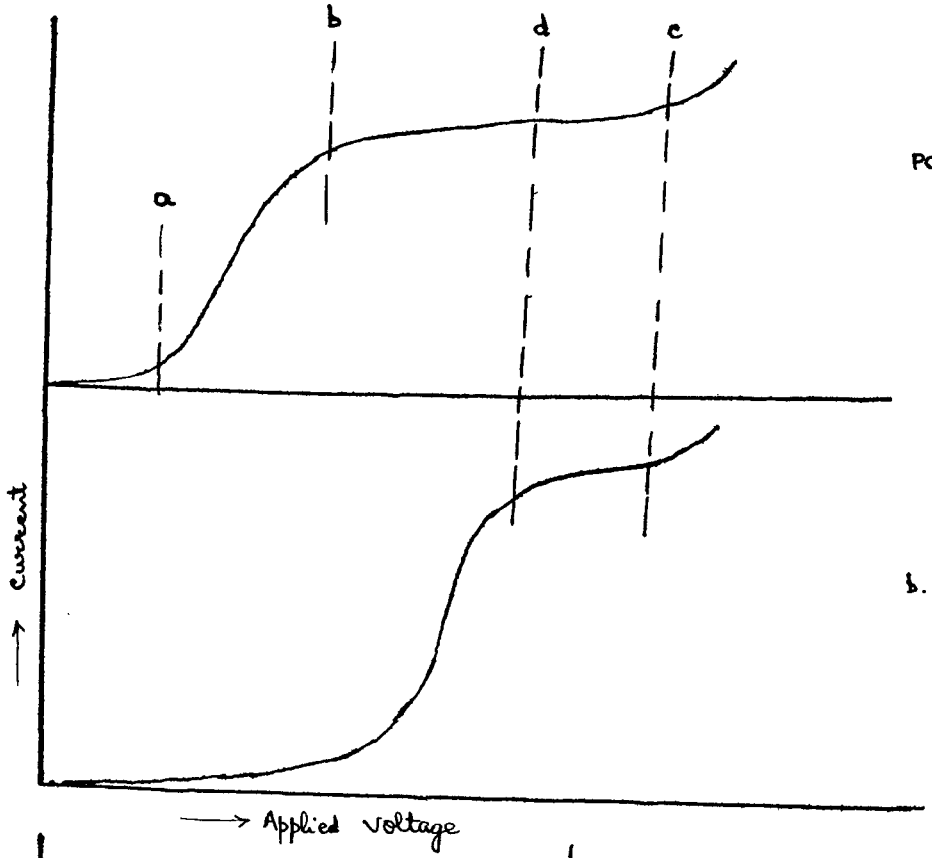
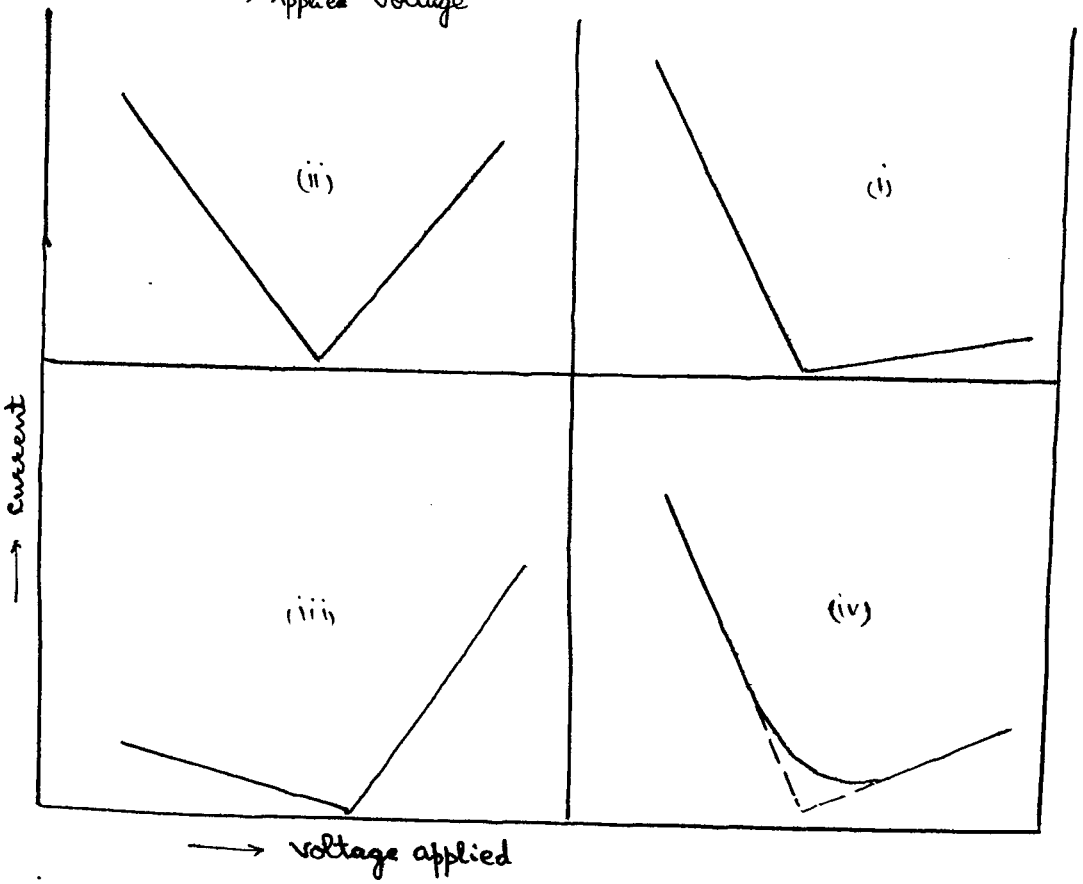


Fig. a
POLAROGRAM OF 'A'

Fig. b
b. POLAROGRAM OF 'B'



(i) When 'A' is titrated against 'B' at potential between b and d.

(ii) For direct and reverse titration at applied potential between c and d.

(iii) For titration of 'B' against A at potential between b and d.

(iv) When the precipitate formed is appreciably soluble.

titrating reagent which is reducible at the dropping mercury electrod

As an illustration consider the titration of a substance A (which gives a polarogram as shown in Fig 7 a) against another substance B (giving a step as in Fig 7b).At the voltage at the diffusion current commences and extends from b to c, it is quite clear that for an applied potential between b and d, curve of the type (i) will be obtained since the excess of B which is added, will not be reduced at this potential. If the potential to be applied is chosen between c and d, a curve of the form (ii) will be obtained since after the complete elimination of A, the reduction of the excess of B added starts and the current increases. Similarly curves of the form (ii) and (iii) will be obtained according to the potential applied when the titration is carried out in the reverse order i.e. B is titrated against A. Sometimes curves of the form (iv) is obtained when the precipitate formed is appreciably soluble. In such cases the extrapolation of the staright past helps in detecting the end point.

The amperometric titrations have got the following main advantages. (i) It is possible to titrate extremly dilute solution with high accuracy than is possible by conductometric or potentiometric methods. (ii) Since the applied voltage is to be kept constant the whole assembly of the apparatus becomes easy. (iii) Only the changes in current (as the potential and conductance in potentiometry and conductometry respectively) and not the actual values, are to be noted during the titration. (iv) Foreign electrolytes which seriously interfere in conductometric titrations cause no interference. (v) The method can be applied in cases where the precipitate

is appreciably soluble, because the measurements are well taken away from the end point which is then found graphically (curve

Amperometric titrations can very well be used in cases where complex formation takes place since the diffusion coefficient of a complex ion differs very much from that of the corresponding simple ion, The potential at which the simple ion gives a diffusion current, but the complex ion is not reduced (since the complex dissociates very slowly at the electrode surface) can be applied for complex formation titrations. In such cases curves of the form (i) or (iii) will naturally be obtained.

In the following pages the experiments on the amperometric titration are described. These have been carried out with a view to confirm my earlier results on the composition and properties of the chromous ferrocyanide complex.

EXPERIMENTAL;

Reagents:-

Pure samples of chromous chloride and potassium ferrocyanide solution were prepared and standardised as described earlier. Normal potassium chloride solution was used as supporting electrolyte and it was prepared from reagent grade sample. Gelatin solution was prepared as described elsewhere and a concentration of 0.005 % was used in all the experiments.

Apparatus:-

Fischer electropode and the titration cell described in earlier chapter were used for the titrations. A multiflex galvanometer type M.G.F. 2 connected externally was used to measure the variations in current.

Procedure:-

The constant potential to be applied for the titrations was first of all determined. Since potassium ferrocyanide is not reduced at the dropping electrode, the anodic wave for chromous chloride was, therefore, taken in IN. potassium chloride and 0.005 % gelatin. 0.5 c.c. of the standardised chromous solution (0.215 M) was transferred from the microburette attachment of the storage flask to the titration cell containing KCl solution and gelatin after complete deaeration. Purified nitrogen was used for deaeration keeping an inert atmosphere throughout the experiment. Increasing potentials were then applied to the cell and the galvanometer readings noted from the c.v. curve plotted. It was found that a voltage in between 0 and -0.3 could be applied for the titrations of chromous chloride against potassium ferrocyanide or vice versa. A potential of -0.2 v was, therefore, chosen for all the experiments. After applying this potential aliquots of potassium ferrocyanide were added to the cell. Readings were taken after each addition and after complete stirring for 2-3 minutes with the help of brisk current of nitrogen. The volume of potassium ferrocyanide added was then plotted against the galvanometer deflection and the end point was determined from the curve.

A concentrated solution of the titrant was always used to avoid any appreciable increase in volume at the end of the titration. Since the diffusion current depends on the concentration of the active ion, a change in volume might bring about a change in the diffusion and hence necessary precaution was taken to avoid this.

Titrations were carried out with varying concentrations

of chromous chloride and also in presence of alcohols. Reverse titrations were carried out both in aqueous and aqueous-alcoholic media by taking potassium ferrocyanide in the electrolytic cell. The results are tabulated as follows:

TABLE 69

1. Volume of 0.215 M $CrCl_2$ used	= 0.5 c.c.
2. Concentration of potassium chloride	= 1 M
3. Concentration of gelatin	= 0.005 %
4. Total volume made up.	= 25 c.c.
.. Concentration of $CrCl_2$	= $\frac{0.215 \times 0.5}{25}$
	= 4.3 m.mole.
5. Drop time (at 1 volt)	= 3.5 sec.
6. Sensitivity of the apparatus	= 5 X
7. Temperature	= 23° C

S. No.	Voltage.	Galv. defln.	Ex No.	Voltage	Galv. defln
1.	0.0	-24.0	9	0.8	0.50
2.	0.1	-24.0	10	0.9	1.00
3.	0.2	-24.0	11	1.0	2.00
4.	0.3	-24.25	12	1.1	2.75
5.	0.4	-20.0	13	1.2	3.25
6.	0.5	-10.0	14	1.3	4.1
7.	0.6	- 1.25	15	1.4	7.5
8.	0.7	0.0	16	1.5	21.0

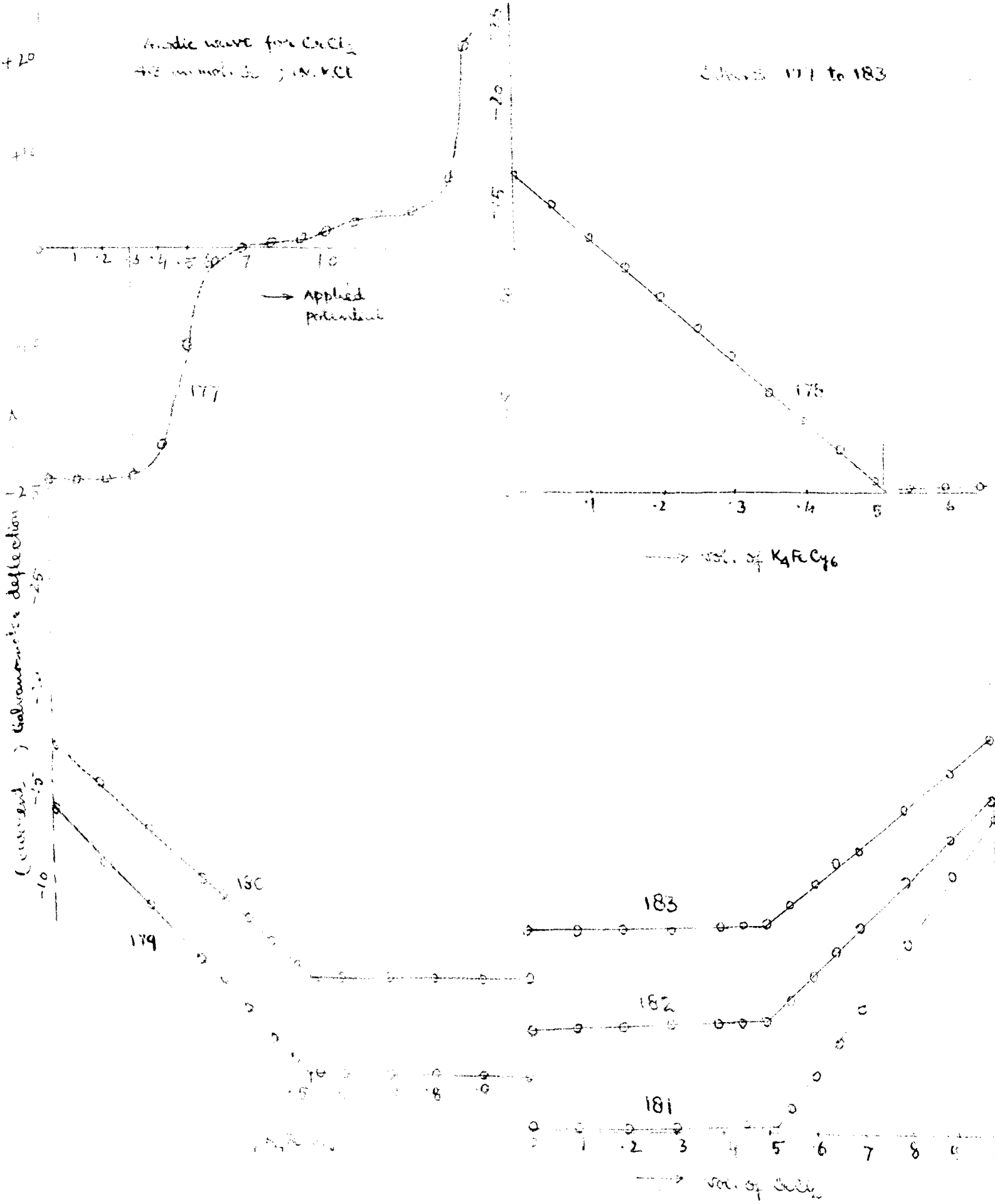
(Vide curve No. 177)

KCl as supporting electrolyte of concentration 1M, 0.005 % gelatin, drop time 3.5 sec. and temperature 23° were kept constant for all the titration experiments, direct as well as reverse. The constant voltage to be applied was determined from the anodic wave. The wave starts at 0.3 volt and hence a safe value of -0.2 volt was applied for all the experiments. The sensitivity switch of the electrode was also kept at a fixed position. 5 X.

AMPEROMETRIC TITRATIONS BETWEEN $CaCl_2$ & K_4FeCy_6

Anodic wave for $CaCl_2$
4·2 m.mols. in 3 c.c. N. KCl

Curves 177 to 183



Readings with $CrCl_2$ in the cell

TABLE CCI

Vol. of 0.215 M $CrCl_2$ = 0.25 c.c.
Vol. of alcohol = 0.0 c.c.
Total volume made up = 25.0 c.c.
% Concentration of $CrCl_2$ = 2.15 n.mol.
Strength of K_4FeCy_6 = 50 n.mol

Vol. of K_4FeCy_6	Galv. deflection
0.0 c.c.	-16.0
0.05 "	-14.75
0.10 "	-13.0
0.15 "	-11.5
0.20 "	-10.0
0.25 "	- 8.5
0.30 "	- 7.25
0.35 "	- 5.25
0.40 "	- 3.75
0.45 "	- 2.25
0.50 "	- 0.75
0.55 "	- 0.25
0.60 "	- 0.25
0.65 "	0.0

(Vide curve No. 178)

25 c.c. 2.15 n.molar $CrCl_2$
= 0.52 c.c. 50. n.molar K_4FeCy_6
= 12.10 c.c. 2.15 n.molar K_4FeCy_6

TABLE CCII

Vol. of 0.215 M $CrCl_2$ = 0.25 c.c.
Vol. of alcohol = 2.0 c.c.
Total volume made up = 25 c.c.
% Concentration of $CrCl_2$ = 2.15 n.m
Strength of K_4FeCy_6 = 50 n.mol

Vol. of K_4FeCy_6	Galv. deflection
0.0 c.c.	-13.5
0.10 "	-11.25
0.20 "	- 9.0
0.30 "	- 6.0
0.35 "	- 5.0
0.40 "	- 3.5
0.45 "	- 2.0
0.50 "	- 1.0
0.55 "	- 0.25
0.60 "	- 0.25
0.70 "	- 0.25
0.80 "	- 0.0
0.90 "	0.0
1.0 "	0.0

(Vide curve No. 179)

25 c.c. 2.15 n.molar $CrCl_2$
= 0.53 c.c. 50. n.molar K_4FeCy_6
= 12.82 c.c. 2.15 n.molar K_4FeCy_6

Readings with $K_4Fe(CN)_6$ in the cell

Table CCIII

Vol. of 0.215 M $CrCl_2$ = 0.25 c.c.

Volume of alcohol = 5 c.c.

Total volume made up = 25 c.c.

∴ Concentration of $CrCl_2$ = 2.15m.mol.

Strength of K_4FeCy_6 = 50 m.mol

Vol. of $K_4Fe(CN)_6$	Galv. deflection
0.0 c.c.	-12.0
0.10 "	-10.0
0.20 "	- 7.75
0.30 "	- 5.0
0.35 "	- 4.25
0.40 "	- 3.25
0.45 "	- 2.0
0.50 "	- 0.75
0.55 "	-0. 25
0.60 "	- 0.25
0.70 "	- 0.25
0.80 "	0.0
0.90 "	0.0
1.0 "	0.0

(Vide curve No. 180)

25 c.c. 2.15 m.molar $CrCl_2$

-0.535 c.c. 50 m.molar $K_4Fe(CN)_6$

= 12.44 c.c. 2.15 m.molar $K_4Fe(CN)_6$

TABLE CCIV

Vol. of 0.1 M $K_4Fe(CN)_6$ = 0.5 c.c.

Volume of alcohol = 0.0 c.c.

Total volume made up = 25 c.c.

∴Conc. of $K_4Fe(CN)_6$ =2 m.mol.

Strength of $CrCl_2$ = 0.204 m.mol.

Vol. of $CrCl_2$	Galv. deflection
0.0 c.c.	0.0
0.10 "	0.0
0.20 "	0.0
0.30 "	- 0.25
0.40 "	- 0.25
0.45 "	- 0.50
0.50 "	- 0.75
0.55 "	- 1.25
0.60 "	- 2.5
0.65 "	- 4.5
0.70 "	- 6.25
0.80 "	- 9.5
0.90 "	-13.0
1.0 "	-16.0

(Vide curve No 181)

25 c.c. 2 m.molar $K_4Fe(CN)_6$

= 0.52 c.c. 20.4 m.molar $CrCl_2$

= 53.04 c.c. 2 m.molar $CrCl_2$

TABLE CCV

Vol. of 0.1 M $K_4Fe(CN)_6$ = 0.5 c.c.

Volume of alcohol = 2.0 c.c.

Total volume made up = 25 c.c.

∴ Conc. of $K_4Fe(CN)_6$ = 2.m.mol

Strength of $CrCl_2$ = 0.204 N

Vol. of $CrCl_2$	Galv. deflection
0.0 c.c.	0.0
0.10 "	0.0
0.20 "	0.0
0.30 "	0.0
0.40 "	-0.25
0.45 "	-0.5
0.50 "	-0.5
0.55 "	-1.5
0.60 "	-2.5
0.65 "	-3.75
0.70 "	-5.5
0.80 "	-7.75
0.90 "	-9.75
1.00 "	-12.0

(Vide curve No. 182)

25 c.c. 2m.molar $K_4Fe(CN)_6$

= 0.50 c.c. 0.204 N $CrCl_2$

= 51.0 c.c. 2.0 m.molar $CrCl_2$

TABLE CCVI

Vol. of 0.1 M $K_4Fe(CN)_6$ = 0.5 c.c.

Volume of alcohol = 5.0 c.c.

Total volume made up = 25 c.c.

∴ Conc. of $K_4Fe(CN)_6$ = 2 m.mol.

Strength of $CrCl_2$ = 0.204 N

Vol. of $CrCl_2$	Galv. deflection
0.0 c.c.	0.0
0.10 "	0.0
0.20 "	0.0
0.30 "	0.0
0.40 "	0.0
0.45 "	-0.25
0.50 "	-0.25
0.55 "	-1.25
0.60 "	-2.5
0.65 "	-3.5
0.70 "	-4.0
0.80 "	-6.25
0.90 "	-8.0
1.00 "	-10.25

(Vide curve No. 183)

25 c.c. 2m.molar $K_4Fe(CN)_6$

= 0.45 c.c. 0.204 N $CrCl_2$

= 45.93 c.c. 2 m.molar $CrCl_2$

It was found from the direct and reverse titrations both in aquous and aquous-alcoholic media, that curves of almost the same nature are obtained except that in the latter case (aquous-alcoholic media) the current was a little suppressed.

For the remaining sets of titrations typical curves have been given instead of the detailed tables. The description along with the titre values are given in the following table:-

TABLE CCVII

(a) Chromous chloride in the cell:

Vol. of $CrCl_2$	Vol. of alcohol	Conc. of $CrCl_2$	Vol. of 0.05 M $K_4Fe(CN)_6$ at the eqvt. point
0.5 c.c.	0.0 c.c.	4.3 m.mol.	1.03 c.c.
0.5 c.c.	2.0 c.c.	4.3 m.mol.	1.04 c.c.
0.5 c.c.	5.0 c.c.	4.3 m.mol.	1.06 c.c.
0.75 c.c.	0.0 c.c.	6.45 m.mol.	1.53 c.c.
0.75 c.c.	2.0 c.c.	6.45 m.mol.	1.55 c.c.
0.75 c.c.	5.0 c.c.	6.45 m.mol.	1.58 c.c.

(b) $K_4Fe(CN)_6$ solution in the cell:

Vol. of $K_4Fe(CN)_6$ (0.1 M)	Vol. of alcohol	Conc. of $K_4Fe(CN)_6$	Vol. of 0.204 M $CrCl_2$ at the eqvt. point.
0.25 c.c.	0.0 c.c.	1.m.mol.	0.255 c.c.
0.25 c.c.	2.0 c.c.	1.m.mol.	0.25 c.c.
0.25 c.c.	5.0 c.c.	1.m.mol.	0.245 c.c.
1.0 c.c.	0.0 c.c.	4.m.mol.	1.08 c.c.
1.0 c.c.	2.0 c.c.	4.m.mol.	1.02 c.c.
1.0 c.c.	5.0 c.c.	4.m.mol.	1.00 c.c.

TABLE CCVIII

(Summary of the readings for direct titrations ($CrCl_2$ in the cell)

Conc. of $CrCl_2$	Percentage of alcohol	Vol. of $CrCl_2$	Conc. of $K_4Fe(CN)_6$	Vol. of $K_4Fe(CN)_6$ eqvt. to $CrCl_2$	Probable ratio $K_4Fe(CN)_6$: $CrCl_2$
2.15 m.mol.	0.0	25 c.c.	0.05 M	12.10	1:2
2.15 m.mol.	8.0	25 c.c.	0.05 M	12.32	1:2
2.15 m.mol.	20.0	25 c.c.	0.05 M	12.44	1:2
4.3 m.mol.	0.0	25 c.c.	0.05 M	11.98	1:2
4.3 m.mol.	8.0	25 c.c.	0.05 M	12.1	1:2
4.3 m.mol.	20.0	25 c.c.	0.05 M	12.32	1:2
6.45 m.mol.	0.0	25 c.c.	0.05 M	11.86	1:2
6.45 m.mol.	8.0	25 c.c.	0.05 M	12.01	1:2
6.45 m.mol.	20.0	25 c.c.	0.05 M	12.25	1:2

TABLE CCIX

Summary of the readings for reverse titrations ($K_4Fe(CN)_6$ in the cell)

Conc. of $K_4Fe(CN)_6$	Percentage of alcohol	Vol. of $K_4Fe(CN)_6$	Conc. of $CrCl_2$	Vol. of $CrCl_2$ eqvt. to $K_4Fe(CN)_6$	Probable ratio $K_4Fe(CN)_6$: $CrCl_2$
1 m.mol.	0.0	25 c.c.	0.102 M	52.02 c.c.	1:2
1 m.mol.	8.0	25 c.c.	0.102 M	51.00 c.c.	1:2
1 m.mol.	20.0	25 c.c.	0.102 M	49.98 c.c.	1:2
2 m.mol.	0.0	25 c.c.	0.102 M	53.04 c.c.	1:2
2 m.mol.	8.0	25 c.c.	0.102 M	51.00 c.c.	1:2
2 m.mol.	20.0	25 c.c.	0.102 M	49.98 c.c.	1:2
4 m.mol.	0.0	25 c.c.	0.102 M	52.02 c.c.	1:2
4 m.mol.	8.0	25 c.c.	0.102 M	52.02 c.c.	1:2
4 m.mol.	20.0	25 c.c.	0.102 M	51.00 c.c.	1:2

Discussion:

The following conclusions can be drawn from the observations on amperometric titrations between chromous chloride and potassium ferrocyanide, carried out both in aquous and aquous-alcoholic media.

1. Both the direct and reverse titrations with various concentrations of chromous chloride and potassium ferrocyanide give evidence for the formation of only one complex of the composition $Cr_2Fe(CN)_6$, potassium ferrocyanide and chromous chloride reacting in the molar ratio 1:2.

2. In the case of direct titrations (with chromous chloride solution in the cell), the titre values are low in aquous medium, but in the presence of alcohol an increase is observed the titre value approaching almost the theoretical value(vide column No. 6 of the summarised table. From these it may be seen that the values rise from 12:1 c.c. to 12.25 c.c. for $CrCl_2$ of 2.15, 4.3 and 6.45 millimolar respectively. This approaching the theoretical value of 12.5 c.c., this may be due to the fact that the presence of alcohol suppresses the adsorption of Cr(ii) by the complex. In aquous medium, the complex formed by the additon of $K_4Fe(CN)_6$ to chromous chloride, holds some of the latter in the adsorbed state making it not easily available for the reaction. The presence of alcohol suppresses this phenomenon and hence the titre value reaches the theoretical value.

3. The concentrations of the reagents also seem to influence the titre values. Better results are always obtained with dilute solution the titre values (volume of ferrocyanide) rising from 11.86 to 12.1 in aquous medium; from 12.01 to 12.32 in presence of 8 % alcohol, and from 12.25 to 12.44 in presence of 20 % alcohol as against 25 cc, of 6.45 and 2.15 millimolar chromous chloride. This is quite expected,

since more bulky precipitates obtained with concentrated solutions will hold more of chromous chloride in the adsorbed state. Moreover, it is also clear from this that hydrolysis plays an insignificant role, if at all, as otherwise a reverse effect would have been observed with dilute solutions.

4. The adsorption of chromous ions by the complex is also supported by the reverse titrations (with potassium ferrocyanide in the cell). the titre values (vide column b of the summarised table No.) are higher than the theoretical in the aquous medium, but come to the normal values in presence of alcohol. The values for 25 c.c. of 1.2 and 4 millimolar potassium ferrocyanide vary from 52.02 to 49.98; 53.04 to 49.98 and 55.8 to 51 c.c. of chromous chloride when the medium is changed from aquous to alcoholic.

The rise in difussion current, after the end point may be due to chromous ions. But this is not realised immediately after the end point since the chromous ions added are held up by the complex. When sufficient excess of the reagent has been added, the current starts rising and hence higher titre values are obtained.

II. ADSORPTIVE AND HYDROLYTIC PROPERTIES OF CHROMOUS FERROCYANIDE.

The conclusions arrived at on the basis of my experiments on the conductometric, potentiometric and amperometric titrations, necessiated further investigations on the adsorption capacity of the freshly precipitated chromous ferrocyanide. A quantitative study of the adsorption of Cr(ii) and $FeCy_6^{4-}$ by the complex both in aquous and aquous alcoholic media, was therefore, taken up. The method employed recently by some workers in the field of heavy metals ferro-and-ferricyanides was used with some modifications. To a volume of chromous chloride calculated to give a known weight of the complex $Cr_2Fe(CN)_6$, increasing amounts of potassium ferrocyanide solution were added in seperate airtight flasks under nitrogen atmosphere. The excess ferrocyanide left after adsorption was estimated after 24 hours and the extent of adsorption was foumd out by plotting curves between equilibrium concentration and the weight in moles per mole of the complex.

Experiments were performed in aquous and aquous alcoholic media. The adorption of chromium was also studied in an exactly simila way as for the ferrocyanogen ions.

Although very little evidence regarding the hydrolysis of the freshly precipitated complex was available, experimets to arrive at some definite conclusion on its hydrolytic behaviour, were also performed. The results on this aspect are discussed in the latter part of this section.

EXPERIMENTAL

Solutions od chromous chloride and potassium ferrocaynide were prepared and standardised as described earlier. An approximately N/20 solution of potassium permanganate was prepared and standardised against decinormal oxalic acid, for the estimation of unadsorbed potassium ferrocyanide. A dilute solution of sodium thiosulphate (N/20) was prepared and standardised iodometrically against 0.1 N potassium dichromate, and this was used for the volumetric estimation of chromium as chromate.

Apparatus:

The experiments had to be carried out under an inert atmosphere to prevent the oxidation of Cr(ii). For this purpose the following arrangements was done. Ten clean conical flasks (250 c.c.) were fitted with three holed rubber corks carrying an inlet tube and an oulet tube. The third hole of the cork was used for adding the adsorbate and was kept closed when not in use. The flasks were arranged in series, connecting the outlet of the first to the inlet of the second and so on, the outlet of the last flask was arranged with a Bunsen valve. Purified nitrogen was used to replace the air and keep an inert atmosphere. It also served as a continuous stirring device throughout the experiment. The flasks were kept in water both at 23°.

Procedure:

Adsorption of K_4FeCy_6. The strength of chromous chloride solution was first of all determined and found to be 0.3073 M, and that of potassium ferrocyanide 0.2 M. The proportion in which these reagents are to be mixed to give a neutral complex was found by trial (vide page) and it was in close agreement with the calculate

values for the complex $Cr_2Fe(CN)_6$. 1 c.c. of 0.2 M $K_4Fe(CN)_6$ required 1.30 c.c. of $CrCl_2$giving a molar ratio of 1:2.

The volumes of the reagents to give 1.0 gm of the complex om mixing, were calculated from the equation.

$K_4Fe(CN)_6 + 2\ CrCl_2 = Cr_2Fe(CN)_6 + 4\ KCl$ as follows:

1000 c.c. of 1 M $K_4Fe(CN)_6$ givesd ------- 1 gm mole. of complex.

$= 315.8$ gm.

∴ Volume of 0.2 M $K_4Fe(CN)_6$ required to give 1.0 gm of the complex. $= \frac{1000}{315.8 \times .2}$

$= 15.83$ c.c.

Volume of 0.2 M CrCl to give 1 gm. complex $= 31.66$ c.c.

.. Volume of 0.3073 M $CrCl_2$ 1 gm. oomplex $= \frac{0.2 \times 31.66}{0.3073}$

$= 20.6$ c.c.

Thus it was found that 15.83 c.c. of 0.2 M $K_4Fe(CN)_6$reacts with 20.6 c.c. of 0.3073 M $CrCl_2$to give 1 gm. of the complex $Cr_2Fe(CN)_6$

The flasksw were arranged in series andafter completely replacing the air by nitrogen (in about an hour), 20.6 c.c. of chromous chloride was transferred to every flask from the storage bottle. 15.83 c.c. of the standard ferrocyanide solution was then added to them, the current of nitrogen being maintained throughout. In this manner 1 gm. of the complex in the freshly precipitated from, was obtained in each flask. Increasing amounts, from 5 to 50 c.c. of 0,2 M potassium ferrocyanide were than added to the flasks and the toatl volume made up to 100 c.c. in every case by air free distilled water The contents were mixed throughly by a rapid current of nitrogen where after it was slowed down and maintained for 24 hours. The flasks were

the disconnected, the supernatant solutions centrifuged and the excess ferrocyanide was estimated by titrating known volumes from it against standard potassium permanganate. The readings are tabulated as follows:

TABLE CCX

Vol. of $CrCl_2$	Vol. of $K_4Fe(CN)_6$	Vol. of water.	Vol. taken for titration .	Titre value (N/20.3 $KMnO_4$).	Total $KMnO_4$ eqvt.
20.6 c.c.	15.83 5 c.c.	58.57 c.c.	20.0 c.c.	1.99 c.c.	9.95 c.c.
20.6 c.c.	15.83 10 c.c.	53.57 c.c.	20.0 c.c.	3.98 c.c.	19.90 c.c.
20.6 c.c.	15.83 15 c.c.	48.57 c.c.	20.0 c.c.	6.26 c.c.	31.30 c.c.
20.6 c.c.	15.83 20 c.c.	43.57 c.c.	20.0 c.c.	8.55 c.c.	42.75 c.c.
20.6 c.c.	15.83 28 c.c.	38.57 c.c.	10.0 c.c.	5.59 c.c.	55.90 c.c.
20.6 c.c.	15.83 30 c.c.	28.57 c.c.	10.0 c.c.	7.03 c.c.	70.30 c.c.
20.6 c.c.	15.83 35.c.c.	28.57 c.c.	10.0 c.c.	8.75 c.c.	87.50 c.c.
20.6 c.c.	15.83 40 c.c.	23.57 c.c.	10.0 c.c.	10.49 c.c.	104.90 c.c.
20.6 c.c.	15.83 45 c.c.	18.57 c.c.	10.0 c.c.	12.16 c.c.	121.60 c.c.
20.6 c.c.	15.83 50 c.c.	13.57 c.c.	10.0 c.c.	14.07 c.c.	140.70 c.c.

Vol. of $KMnO_4$ equivalent to 50 c.c. of $K_4Fe(CN)_6$ = 20.3 c.c.

From the above readings, the total volume of $KMnO_4$ which would have been required if adsorption had not taken place, was calculated in each case and hence the volume equivalent to the amount K_4FeCy_6 adsorbed. The equivalent concentration of ferrocyanide was calculated in each case in millimoles per litre and also the amount of it adsorbed in moles per mole of the complex. It is illustrated for one set as follows:

Normality of $KMnO_4$ = N 120.3

Volume of $KMnO_4$ for 20 c.c. solution = 1.99 c.c.

$\therefore$ Normality of supernatent solution = $\frac{1.99}{20.3 \times 20}$

$\therefore$ Conc. of $K_4Fe(CN)_6$ in millimoles per litre = $\frac{1.99 \times 1000}{20.3 \times 20}$ = 4.901

Adsorption:

Volume of $KMnO_4$ for 20 c.c. solution = 1.99 c.c.

$\therefore$ Volume of $KMnO_4$ for the total solution = (100 c.c.) = 0.95 c.c.

Volume of $KMnO_4$ which would have been required if there was no adsorption = 20.3 c.c.

$\therefore$ Volume of $KMnO_4$ equivalent to the amount of $K_4Fe(CN)_6$ adsorbed = 10.35 c.c.

$\therefore$ The weight of $K_4Fe(CN)_6$ adsorbed = $\frac{422.2 \times 10.35}{20.3 \times 1000}$

Molecular weight of complex = 315.8

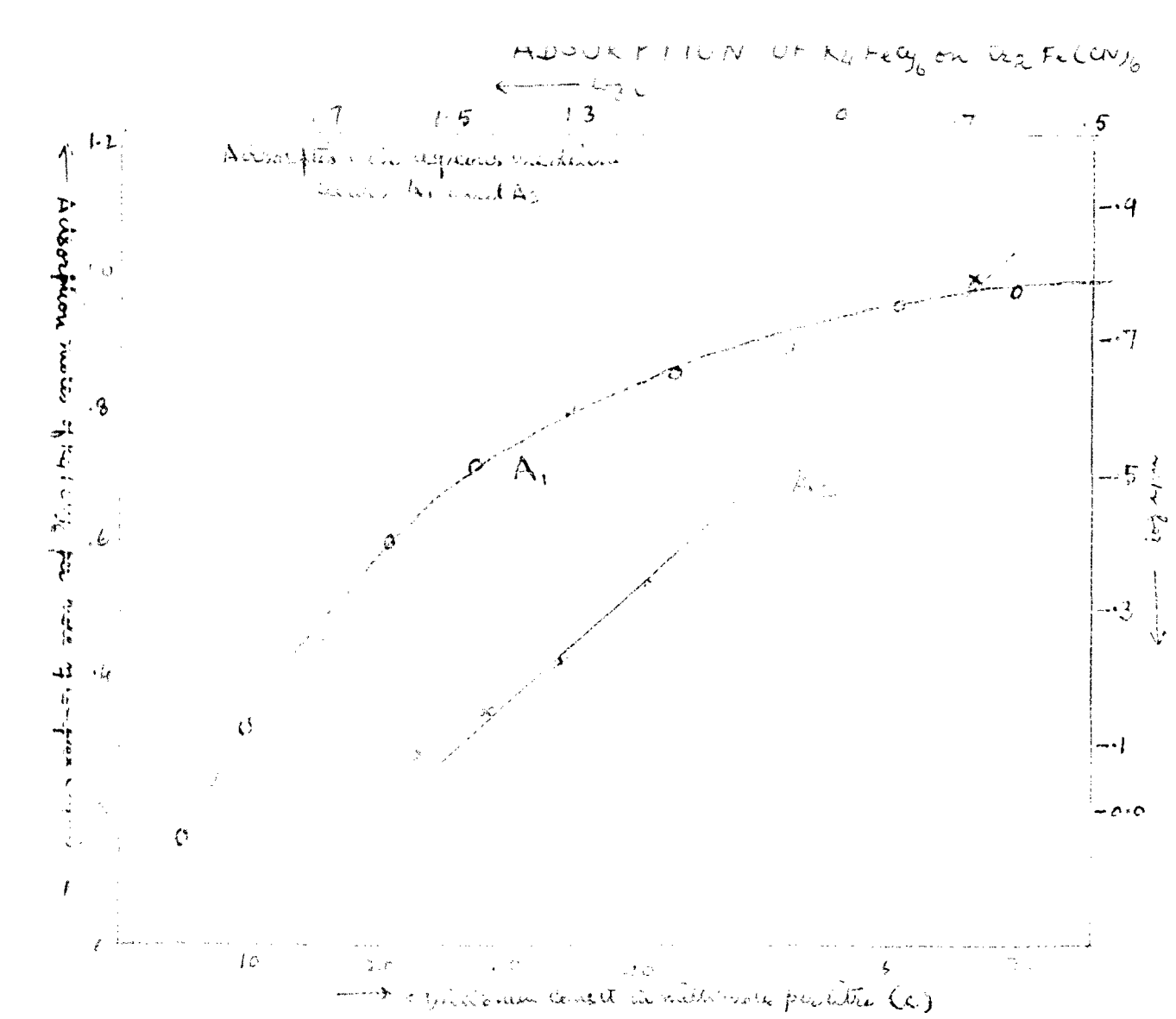
$\therefore$ the amount of $K_4Fe(CN)_6$ adsorbed in moles/mole of the complex = $\frac{10.35 \times 315.8}{20.3 \times 1000} = 0.1610$

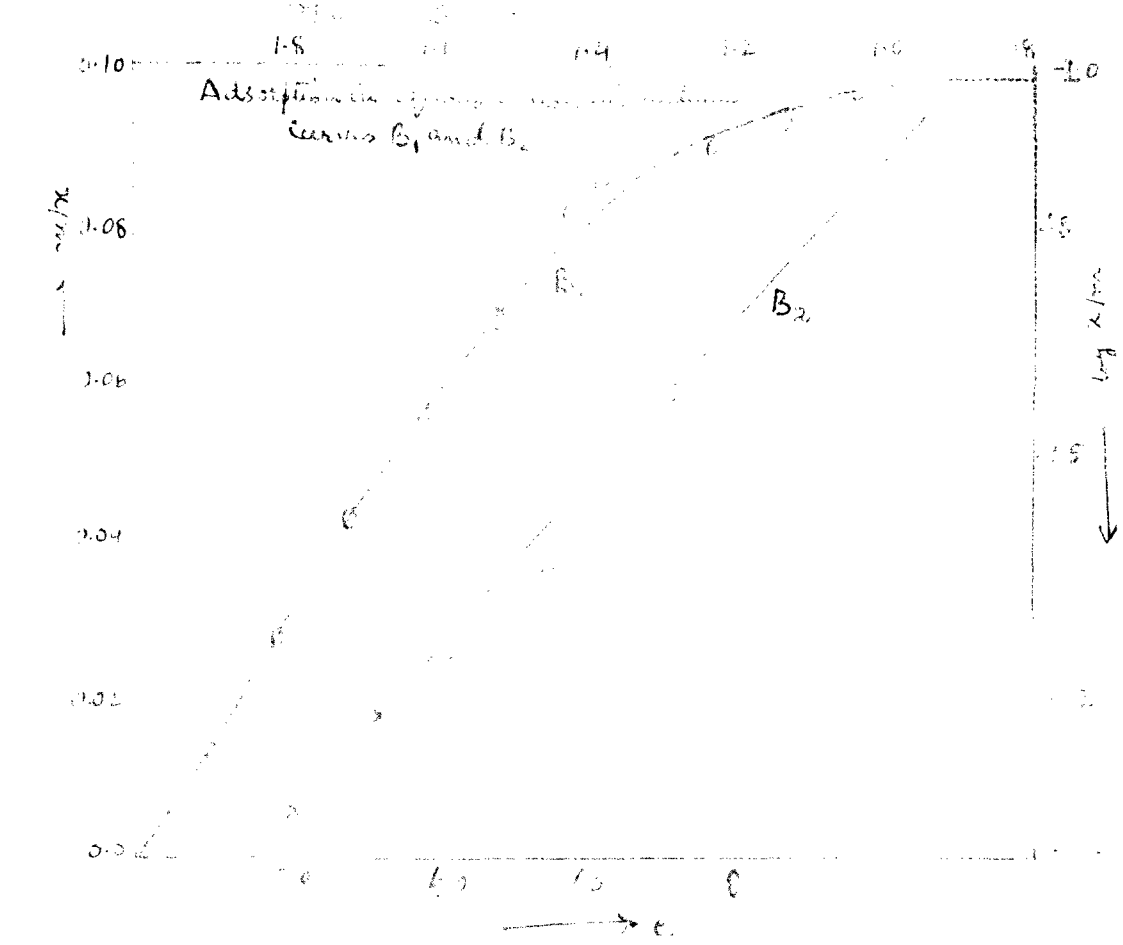
The calculations were done in every case as described above. The results for the different sets are tabulated below:

TABLE CCXI

Vol. of $KMnO_4$ eqvt. after adsorption	Vol. of $KMnO_4$ eqvt. before adsorption	Vol. of $KMnO_4$ eqvt. to $K_4Fe(CN)_6$ adsorption	Eqbm.Conc. (millimoles)	Adsorption (Moles/moles complex
9.95 c.c.	20.3 c.c.	10.35 c.c.	4.901	001610
19.90 c.c.	40.6 c.c.	20.70 c.c.	9.804	0.3220
31.30 c.c.	60.9 c.c.	29.60 c.c.	15.42	0.4602
42.75 c.c.	81.2 c.c.	38.45 c.c.	21.06	0.5980
55.90 c.c.	101.5 c.c.	45.60 c.c.	27.54	0.7092
70.30 c.c.	121.8 c.c.	51.50 c.c.	34.63	0.8010
87.50 c.c.	142.1 c.c.	54.60 c.c.	43.10	0.8492
104.90 c.c.	162.4 c.c.	57.50 c.c.	51.66	0.8905
121.60 c.c.	182.7 c.c.	61.10 c.c.	59.89	0.9510
140.70 c.c.	203.0 c.c.	62.30 c.c.	69.29	0.9691

The equilibrium concentration was plotted against adsorption (vide curve No A$_6$) and from the graph the maximum adsorption was found out by the extrapolation method. The logarithm of the equilibrium


ADSORPTION OF $K_4Fe(CN)_6$ ON $Cu_2Fe(CN)_6$
Adsorption curves for aqueous solutions
curves A_1 and A_2
A_1
A_2
Adsorption x/m in gm. per gm.
$\log x/m$
$\log c$
Equilibrium concentration (c.)


Adsorption
curves B_1 and B_2
B_1
B_2
x/m
$\log x/m$
$\log c$
c.

concentration was also plotted against log adsorption(curve No A_2) and was found to give a straight line for lower concentrations. The maximum adsorption as obtained from curve No. A_1 was found to be 0.99 mole of $K_4Fe(CN)_6$ per mole of the complex $Cr_2Fe(CN)_6$.

The adsorption of potassium ferrocyanide by the complex in aquous alcoholic media was carried out in a similar way as in aquous media except that 10.0 c.c. of alcohol was added to each flask after the precipitation of the complex and prior to the addition of the excess ferrocyanide. This gave a concentration of 10% alcohol in the mixture. More concentrated solutions of $K_4Fe(CN)_6$ for studying adsorption, in presence of alcohol, was avoided due to precipitation of the electrolyt The results are summarised in the following table.

TABLE CCXII

Volume of alcohol added in every case = 10 c.c.

Vol. of $CrCl_2$	Vol. of K_4FeCy_6	Vol. of water	Vol. taken for titration	Titre value (N/20.3 $KMnO_4$)	Total $KMnO_4$ eqvt.
20.6 c.c.	15.83 5 c.c.	48.57 c.c.	20.0 c.c.	3.9 c.c.	19.5 c.c.
20.6 c.c.	15.83 10 c.c.	48.57 c.c.	20.0 c.c.	7.77 c.c.	38.85 cc.
20.6 c.c.	15.83 15 c.c.	38.57 c.c.	20.0 c.c.	11.64 c.c.	58.20 cc.
20.6 c.c.	15.83 20 c.c.	33.57 c.c.	10.0 c.c.	7.76 c.c.	77.6 c.c.
20.6 c.c.	15.83 25 c.c.	28.57 c.c.	10.0 c.c.	9.72 c.c.	97.2 c.c.
20.6 c.c.	15.83 30 c.c.	23.57 c.c.	10.0 c.c.	11.66 c.c.	116.6 c.c.
20.6 c.c.	15.83 35 c.c.	18.57 c.c.	10.0 c.c.	12.66 c.c.	126.6 ccc.
20.6 c.c.	15.83 40 c.c.	13.57 ccc.	10.0 c.c.	15.67 c.c.	156.7 c.c.
20.6 c.c.	15.83 45 c.c.	8.57 c.c.	5.0 c.c.	8.84 c.c.	176.8 c.c.
20.6 c.c.	15.83 50 c.c.	3.57 c.c.	5.0 c.c.	9.84 c.c.	196.8 c.c.

The equilibrium concentration and the adsorption of $K_4Fe(CN)_6$ in moles per mole of the complex were calculated and the results are given on the next page.

TABLE CCXIII

Vol. of $KMnO_4$ after adsorption	Vol. of $KMnO_4$ before adsorption	Vol. of $KMnO_4$ aquivalent to K_4FeCy_6 adsorbed	Eqvt. Conc. (in millimoles)	Adsorption in moles per complex
19.5 c.c.	20.3 c.c.	0.80 c.c.	9.828	0.0125
38.85 c.c.	40.6 c.c.	1.75 c.c.	19.14	0.0274
58.20 c.c.	60.9 c.c.	2.70 c.c.	28.67	0.0420
77.6 c.c.	81.2 c.c.	3.60 c.c.	38.23	0.0556
97.2 c.c.	101.5 c.c.	4.30 c.c.	47.88	0.0670
116.6 c.c.	121.8 c.c.	5.20 c.c.	58.45	0.0809
126.6 c.c.	142.1 c.c.	5.50 c.c.	62.09	0.0854
156.7 c.c.	162.4 c.c.	5.70 c.c.	77.20	0.089
176.8 c.c.	182.7 c.c.	5.90 c.c.	87.10	0.0925
196.8 c.c.	203.3 c.c.	6.20 c.c.	96.96	0.097

The plots were made as in the previous case and from the graph the maximum adsorption was found out by the extrapolation method

The maximum adsorption in presence of 10% alcohol was found to be o.098 moles of $K_4Fe(CN)_6$ per mole of the complex. The log plot gave a straight line for lower concentrations.

Adsorption of chromous ions:

I gm. of the neutral complex in each flask, was precipitated in the manner already. Increasing amounts, from 2.5 c.c. to 25 c.c., of chromous chloride were then added to the flasks and the total volum made up to 100 c.c. with air free distilled water. The contents were then mixed throughly by a rapeid current of nitrogen and allowed to remain for 24 hours. The slow current of nitrogen was maintained throughout in order to keep an effective inert atmosphere and also to keep the contents stirring. The flasks were then disconnected, the supernatent solutions centrifuged and the excess chrmium was estimate volumetrically, in each case converting a known volume of it into chromate and titrating in the acid medium against standard thiosulphate.

TABLE CCXIV

Strength of thiosulphate = 0.052 N.

Vol. of $K_4Fe(CN)_6$	Vol. of $CrCl_2$	Vol. of water	Vol. taken for estimation	Titre value ($Na_2S_2O_3$)	Total thiosulphate equivalent.
15.83 c.c.	20.6- 2.5 c.c.	62.07 c.c.	10.0 c.c.	2.59 c.c.	25.9 c.c.
15.83 c.c.	20.6- 5.0 c.c.	58.57 c.c.	10.0 c.c.	6.22 c.c.	62.2 c.c.
15.83 c.c.	20.6- 7.5 c.c.	56.07 c.c.	10.0 c.c.	9.86 c.c.	98.6 c.c.
15.83 c.c.	20.6- 10.0 c.c.	53.57 c.c.	10.0 c.c.	13.91 c.c.	139.6 c.c.
15.83 c.c.	20.6- 12.5 c.c.	51.07 c.c.	5.0 c.c.	8.96 c.c.	179.2 c.c.
15.83 c.c.	20.6- 15.0 c.c.	48.57 c.c.	5.0 c.c.	11.01 c.c.	220.2 c.c.
15.83 c.c.	20.6- 17.5 c.c.	46.07 c.c.	5.0 c.c.	13.11 c.c.	262.2 c.c.
15.83 c.c.	20.6- 20.0 c.c.	43.57 c.c.	2.0 c.c.	6.09 c.c.	304.5 c.c.
15.83 c.c.	20.6- 22.5 c.c.	41.07 c.c.	2.0 c.c.	6.96 c.c.	347.8 c.c.
15.83 c.c.	20.6- 25.0 c.c.	38.57 c.c.	2.0 c.c.	7.82 c.c.	391.0 c.c.

Volume of thiosulphate for 1 c.c. original $CrCl_2$solution = 17.75 c.c.

From the above readings, the total volume of thiosulphate which would have been required if adsoption had not taken place and the volume of thiosulphate equivalent to the chromous chloride were calculated in each case. The equilibrium concentration of chromous ions was calculated in millimoles per litre and the amount of it adsorbed in moles per mole of the complex.

Taking first set,

Normality of thiosulphate used = 0.052 N

Volume of supernatent solution taken = 10 c.c.

Volume of thiosulphate required = 2.59 c.c.

$\therefore$ Concentration of chromium in millimoles (i.e. equilibrium concentration)

$$= \frac{2.59 \times 0.052}{10} \times \frac{1}{3} \times 1000$$

$$= 4.489$$

Adsorption:

Weight of complex(adsorbent) = 1 gm.

Volume of thiosulphate for 10 c.c. supernatent solution. = 2.59 c.c.

∴ Volume of thiosulphate the equivalent to the total solution(100 c.c.) = 25.9 c.c.

Volume of thiosulphate which would have been required if there was no adsopption. = 2.5 x 17.75 = 44.375 cc.

∴ Volume of thiosulphate equivalent to the amount of chromium adsorbed. = 18.475c.c.

∴ The amount of chromium adsorbed in mole $= \frac{18.48 \times 0.052}{1000} \times \frac{1}{3}$

$= X$

The amount of Cr adsorbed in moles per mole of the complex = X x 315.8 = 0.1012

The calculations were done in every case as above and the results tabulated as follows:

TABLE CCXV

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Vol. of $Na_2S_2O_3$ eqvt. after adsorption	Vol. of $Na_2S_2O_3$ eqvt. before adsorption	Vol. of $Na_2S_2O_3$ eqvt. to Cr adsorbed	Equilibrium concentration (in m.moles)	Adsorption in moles per mole complex
25.9 c.c.	44.37 c.c.	18.47 c.c.	4.489	0.1012
62.2 c.c.	88.74 c.c.	26.54 c.c.	10.78	0.1451
98.6 c.c.	133.11 c.c.	34.51 c.c.	17.09	0.1885
139.1 c.c.	177.48 c.c.	38.38 c.c.	24.11	0.2100
178.2 c.c.	221.85 c.c.	42.65 c.c.	31.07	0.2355
220.2 c.c.	266.22 c.c.	46.02 c.c.	38.17	0.2520
262.2 c.c.	310.59 c.c.	48.39 c.c.	45.44	0.2651
304.5 c.c.	345.96 c.c.	50.46 c.c.	52.78	0.2730
347.8 c.c.	399.33 c.c.	51.53 c.c.	60.29	0.2820
391.0 c.c.	443.70 c.c.	52.70 c.c.	67.78	0.2871

The equilibrium concentration was plotted against adsorption (vide curve no. C_1) and from the graph the maximum adsorption was found out by extrapolation method. The logarithm of equilibrium concentration was also plotted against log. adsorption (curve no. C_2) and was found to give a straight line.

The extent of adsorption as observed from curve no. C_1 was found

to be 0.295 mole of chromium per mole of the complex $Cr_2Fe(CN)_6$.

The adsorption of chromous ions by the complex in presence of alcohol, was carried out in a similar way as for the aquous media except that 10 c.c. of alcohol was added to the reaction flasks after the precipitation of the complex and prior to the addition of the excess chromous chloride. This gives a concentration of 10% alcohol in the mixture after making upto 100 c.c.

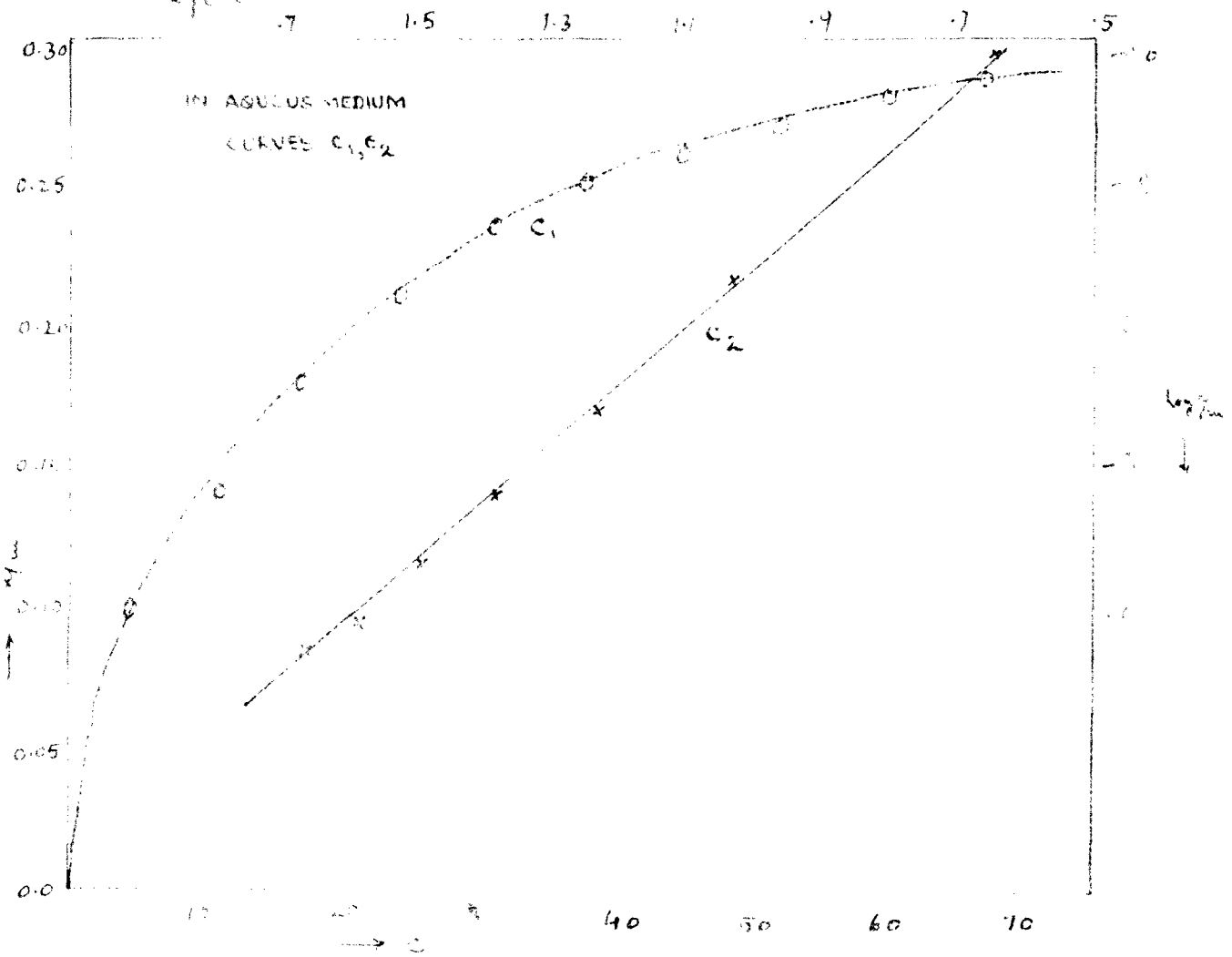
The results are summarised in the following table:-

TABLE CCXVI

Vol. of $K_4Fe(CN)_6$	Vol. of $CrCl_2$	Vol. of water	Vol. taken for estimation	Titre value	Total thiosulphate equivalent.
15.83 c.c.	20.6- 2.5 c.c.	51.07 c.c.	10 c.c.	422 cc.	42.00 cc.
15.83 c.c.	20.6- 5.0 c.c.	48.57 c.c.	10.c.c.	8.36 cc.	83.6 cc.
15.83 c.c.	20.6- 7.5 c.c.	46.07 c.c.	10 c.c.	12.5 cc.	125.1 cc.
15.83 c.c.	20.6-10.0 c.c.	53.57 c.c.	5.0,c,	8.37 cc.	167.4 cc.
15.83 c.c.	20.6-12.5 c.c.	51.07 c.c.	5.c.c.	10.48 cc.	209.4 cc.
15.83 c.c.	20.6-15.0 c.c.	48.57 c.c.	5 c.c.	12.58 cc.	251.6 cc.
15.83 c.c.	20.6-17.5 c.c.	46.07 c.c.	2 c.c.	5.90 cc.	295.0 cc.
15.83 c.c.	20.6-20.0 c.c.	43.57 c.c.	2.ccc.	6.77 cc.	338.5 cc.
15.83 c.c.	20.6-22.5 c.c.	41.07 c.c.	2.c.c.	7.64 cc.	382.0 cc.
15.83 c.c.	20.6-25.0 c.c.	38.57 c.c.	2 c.c.	8.51 cc.	425.5 cc.

The equilibrium concentration and the amount of chromium adsorbed in mole of the complex were calculated in each case. The results are tabulated in the next page.

ADSORPTION OF



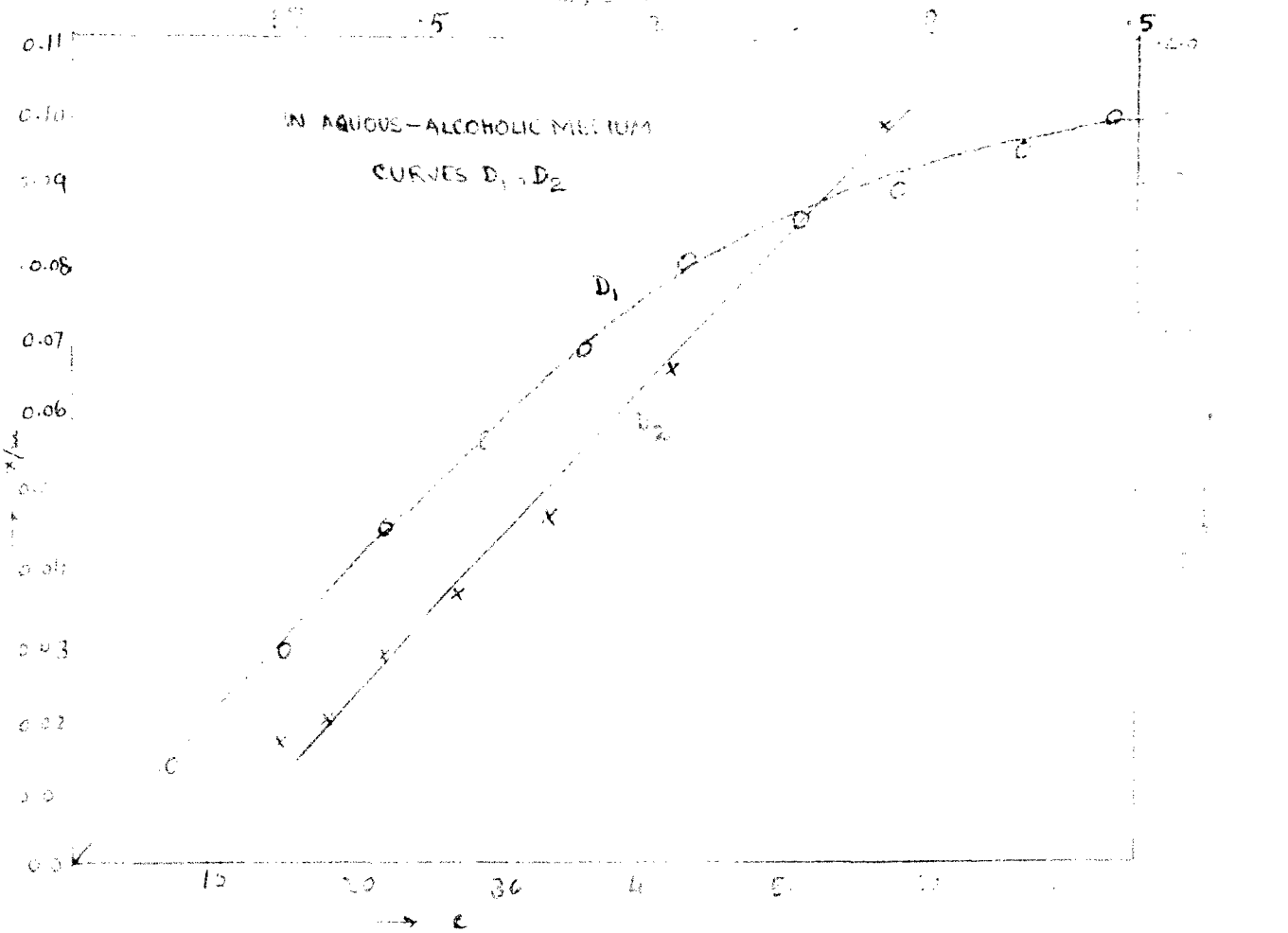


TABLE CCXVII

Vol. of $Na_2S_2O_3$ eqvt.	Vol. of $Na_2S_2O_3$ eqvt. before adsorption	Vol. of $Na_2S_2O_3$ eqvt. to Cr adsorbed	Equilibrium concentration (in millimoles)	Adsorption in moles per mole complex
42.0 c.c.	44.37 c.c.	2.37 c.c.	7.28	0.0128
83.6 c.c.	88.74 c.c.	5.14 c.c.	14.49	0.0280
125.1 c.c.	133.11 c.c.	8.01 c.c.	21.68	0.0437
167.4 c.c.	177.48 c.c.	10.08 c.c.	29.02	0.0552
209.6 c.c.	221.85 c.c.	12.25 c.c.	36.34	0.0670
251.6 c.c.	266.22 c.c.	14.62 c.c.	43.61	0.0800
295.0 c.c.	310.59 c.c.	15.59 c.c.	51.13	0.0852
338.5 c.c.	354.96 c.c.	16.46 c.c.	58.59	0.0898
382.0 c.c.	399.33 c.c.	17.33 c.c.	67.14	0.0948
425.5 c.c.	443.70 c.c.	18.2 c.c.	73.67	0.0995

The equilibrium concentration was plotted against adsorption (vide curve no. D_1) and from the graph the maximum adsorption was found out by the extrapolation method. The logarithm of adsorption was also plotted against log. (curve no. D_2)

The extent of adsopption in aquous-alcoholic media was formed to be 0.102 mole of phromium per mole of the complex.

Hydrolytic behaviour of the complex.

The method usually employed for determining the hydrolysis of such complexes(loc.cit) is to use concentrated sols of the compound. In my case since only a very dilute sol could be obtained, the following prodedure was adopted.

1 gm.'neutral' complex was precipitated in a 25o c.c. flask(vide page 184) and the total volume made up 100 c.c. The supernatent solution was tested for and found to be free from any $FeCy_6^{-4}$ ion. This suspension of the complex was then kept in a

thermostat at 23± 0.1° and was continually stirred for 3 hours by an electric stirrer. The supernatent solution was then centrifuged and 25.0 c.c. of it titrated against N/98.4 potassium permanganate. 0.2 cc. of the permanganate changed the colour of the solution pink showing thereby that even appreciable amount of ferrocyanogen was not liberated by hydrolysis. The experiment was repeated in 55° and also at higher dilution (0,5 and 0.25 gm. of the complex suspended in 100 c.c. of water). The hydrolysis, though small, was found to be enhanced at higher temperatures and with dilution. The summary of the results on hydrolysis at different temperatures and dilutions are given as follows:-

TABLE CCXVIII

Conc. of the complex in suspension gm./100 c.c.	Vol. of N/98.4 $KMnO_4$ eqvt. tp free $FeCy_6$ in total solution	Total amount of $Fe(CN)_6^{4-}$ in suspension	Amount of $FeCy_6^{4-}$ released	Percentage hydrolysis
Temperature 23 ± 0.1°C				
1.0 gm.	0.8 c.c.	0.671 gm.	0.1722 x 10^{-2} gm.	0.2566%
0.5 gm.	0.48 c.c.	0.3355 gm.	0.1034 x "	0.3080%
0.25 gm.	0.40 c.c.	0.1678 gm.	0.0861 x "	0.5131%
Temperature 55 ± 0.1°C				
1.0 gm.	3.25 c.c.	0.6730 gm.	0.6995 x 10^{-2} gm.	1.042 %
0.5 gm.	2.20 c.c.	0.3355 gm.	0.4735 x "	1.411 %
0.25 gm.	1.40 c.c.	0.1678 gm.	0.3013 x "	1.796 %

The last column gives the percentage hydrolysis of the complex and it is seen that it is negligibily small even at the temperature of 55° . It is, however, seen that hydrolysis of the complex takes place appreciably at higher tenperature and greater dilution.

Discussion.

The experiments on the adsorption and hydrolytic properties of chromous ferrocyanide complex, $Cr_2Fe(CN)_6$ lead to the following conclusions:-

The complex has got a great tendency to adsorb both $K_4Fe(CN)_6$ and chromium, the former being to a greater extent than the latter.

It is further seen that the adsorptive capacity of the complex is very much suppress ed by the presence of alcohol.

The maximum adsorption of $K_4Fe(CN)_6$ in the aquous medium is found to be about one (0.99) mole per mole of $Cr_2Fe(CN)_6$. The composition of the complex state can be written as $Cr_2Fe(CN)_6$. $K_4Fe(CN)_6$ which apparently coincides with the formula $K_2CrFe(CN)_6$. This is quite possible since evidence for the formation of $K_2CrFe(CN)_6$ in the freshly precipitated state has been obtained by analytical potentiometric and conductometric methods. Moreover, this shows that the ' adsorption ' of potsssium ferrocyanide is not merely a physical one as could also be seen from the fact that all the adsorbed $K_4Fe(CN)_6$ is not washed off from the complex precipitated from excess of the reagent (vide page 184).

In presence of 10 % alcohol, the maximum adsorption is found to be only 0.098 mole $K_4Fe(CN)_6$ per mole of the complex,

i.e. nearly one tenth of that in aqueous medium. The surface of th e complex may be taken as the means providing an interface of large area at which a solute capable of lowering the interfacial tension. may be accumulated. Water has a much higher air-liquid interfacial tension than for alcoholic solution and accordingly adsorption from the aqueous solution should be greater than in the latter case.

The maximum adsorption of chromium is found to be 0.295 and 0.102 mole per mole of the complex in aqueous medium and in presence of 10% alcohol respectively. The adsorption of chromous ions by the complex is found to be little when compared to that of potassium ferrocyanide. Alcohol suppresses the adsorption of chromium(ii) also as in the case of $K_4Fe(CN)_6$, but to a lesser extent.

On the basis of the experiments carried out to study hydrolysis it can be concluded that this phenomenon plays a minor role in deciding the nature and composition of the complex. A perusal of the last column of table No. 218 (page 257) shows that at ordinary temperature the hydrolysis is quite negligible, being only 0.5 % of the toatal concentration of the complex in 3 hours even with a very dilute suspension (0.25 gm. in 100 cc. water). At 55° with a suspension of 1 gm. of the complex in 100 c.c. water, the percentage hydrolysis is 1.042 and it increases with dilution. The hydrolytic process may be represented in the following two stage

$$Cr_2Fe(CN)_6 + 2\ H_2O \longrightarrow H_2CrFe(CN)_6 + Cr(OH)_2$$

$$H_2CrFe(CN)_6 + 2\ H_2O \longrightarrow H_4Fe(CN)_6 + Cr(OH)_2$$

$$2\ Cr(OH)_2 + H_2O + O \longrightarrow 2\ Cr(OH)_3$$

The chromous hydroxide formed being oxidised to Cr(iii) state. It

On plotting the graph between $\frac{x}{m}$ and c ($\frac{x}{m} = Kc^{1/m}$) curves parabolic in nature, agrreeing with the classical adsorption isotherm $\frac{x}{m} = Kc^{1/m}$ are obtained in every case. At higher concenrations the curves tends to become a straight line parallel to the concenration axis. The maximum adsorption was found out from this part of the curve. The plot between log $\frac{x}{m}$ and log c gives a straight line for the parabolic part of the curve, that is, for lower concentrations of the reagent adsorbed.

From the above it is evident that the experiments on the adsorption and hydrolytic behaviour of the freshly precipitated complex lend support to the results on the composition arrived at on the basis of analytical and other physico-chemical methods.

General Discussion on Chromous Ferrocyanide:

The physico-chemical studies on the products obtained by the interaction of chromous chloride and potassium ferrocyanide, described in the foregoing pages, have conveyed some new and useful information regarding the stabilisation of Cr(ii) and the comparative utility of the methods for investigating their composition. The extent to which success has been achieved in this direction on the basis of chemical and electrometric data, and with the help of adsorption and hydrolysis experiments, can be adjudged from the following short discussion.

From the results on the conductometry, potentiometry and amperometry it can be safely concluded that two definite complexes of cr(ii) having the compositions, $K_2CrFeCy_6$ and Cr_2FeCy_6 exist, although the formation of a complex the formula $K_2Cr_3[FeCy_6]_2$ cannot be ruled out on the basis of chemical analysis. Not cosidering the merits and demerits of the latter method at this stage, it is intresting to find that the more recent and accurate technique of amperometry fails to prove the existance of the complex $K_2CrFeCy_6$ for this reaction——a phenomenon so well demonstrated by other methods and on the basis of adsorption experiments. It can, therefore be argued that the conductometric and potentiometric methods still have not outlived their utility and should be used along with other electrometric methods in having a clear picture regarding the composition of the complexes. It is rather intresting to find that the breaks for Cr_2FeCy_6 were not distinct in potentiometry and conductometry but could be realised distinctly by the amperometric

titrations.

The problem of the structure of Prussian blue and other related compounds has been well discussed by Emeleus and Anderson. According to them prussian blue affords a typical example of the polymerisation of an inorganic molecule and that the product of interaction between ferric chloride and potassium ferrocyanide and ferrous ion and ferricyanide ion should be represented as $Fe\{Fe(FeCy_6)\}$ and $Fe'Fe(FeCy_6)'_2$. Arguing on similar lines and with the support of physico-chemical methods, it was also concluded that copper ferrocyanide is not Cu_2FeCy_6 but $Cu\{Cu(FeCy_6)\}$ that is, the salt of ploynuclear complex anion $\{Cu(FeCy_6)\}^{''}$.

The formulae of the two complexes, as found by different methods, are $Cu_2[Fe(CN)_6]$ and $K_2Cu[Fe(CN)_6]$. Assuming that super-complexes are formed in this case also, chromous ferrocyanide should be represented as (i) $K_2[Cr(FeCy_6)]$ and (ii) $Cr[Cr(FeCy_6)]$. Although physical data, like X-ray and magnetic measurement are not available for these complexes (and probably not known for a majority of heavy metal ferrocyanide), theoretical considerations support this type of structure. Applying the atomic orbital method, it may be that there are four electrons in the 3rd orbitals and this should result in $3d^2\ 4s\ 4p^3$ hybridisation in order to form a cyano-complex with co-ordination number six. Two electrons should remain unpaired in the unhybridised orbitals thereby making the anion paramagnetic in character. As for the possibility of formation of the polynuclear complex anion $\{Cr(FeCy_6)\}^{--}$, bridging between Fe and Cr through the $(CN)_2$ radical can be clearly seen. The crystal structure of the simple unit may be assumed to approximate as in each

$FeCy_3$ surrounded by six chromous ions and each Cr(ii) by six ferrocyanogen radicals. No proof for the existence of the complex $K_2[Cr_3(FeCy_6)_2]$ can, however, be found on considerations discussed above, Chromium, in all its valence states, lacks the suitable orbitals for hexavalent co-ordination and a behaviour as shown by Zn, Ni, or even by Cu should not be expected here. On the other hand my reslts on chemical analysis, atleast in one case, do shown the existance of a complex with the formula $K_2Cr_3(FeCy_6)_2$

That the stabilisation of Cr(ii) has been achieved by complexing with potassium ferrocyanide can now be seen. Besides what has been said in the precceding paragraphs, some other facts also support this view. The complex is very stable can be seen from its properties and the action of acids and alkalis on it(vide page 185). The potential of the change $[Co(CN)_6]^{-4} \rightleftharpoons [Cr(Cy_6)]^{-3}$ is 1.28 V. This value suggests that $CrCy_6^{-3}$ should be stabilised with respect to the $CrCy_6^{-4}$ and hence covalent bound formation with the cyanogen is not able to stabilise Cr(ii) as is seen for Co(ii) or V (ii). This purpose, however, is very well served by the ferrocyanogen complex.

Confirmation to what has been discussed about the composition and structure of chromous ferrocyanide is forthcoming from the experiments on the hydrolysis and adsorption of the complex. The freshly precipitated complex is hydrolysed to a very little extent even at higher temperatures and greater dilutions (vide page 256). This again shows that the complex is stable. Representing hydrolysis as $Cr_2FeCy_6 + 2H_2O = H_2CrFeCy_6 + Cr(OH)_2$ and $H_2CrFeCy_6 + 2H_2O = H\ FeCy + Cr(OH)$ also justified on assuming the existence of

polynuclear complexion anion $[CrFeCy_6]^{---}$. The complex is enourmously endowed with adsorptive capacities (both for Cr(ii) and $FeCy_6^{----}$) is evident from the titration as well as adsorption results. The tendency is so large that about one mole of K_4FeCy_6 per mole of Cr_2FeCy_6 can be made to adsorb under suitable conditions.

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PART II

SOME ASPECTS OF THE PHYSICO-CHEMICAL BEHAVIOUR OF UNSTABLE COBALT COMPOUND—POTASSIUM CYANOCOBALTATE(ii).

INTRODUCTION

The members of the first triad of group VIII in the periodic table are referred to as 'ferrous metals' and include iron, cobalt and nickel. These three elements enter into various complex radicals forming a number of complicated compounds such as the double cyanide and metallic ammines, nickel showing less tendency than the other two. As expected of group VIII elements, to some extent they also give a different varieties of compounds with different valencies, this property being less prominent with cobalt and nickel.

The most important oxidation state of cobalt are II and III Compounds of cobalt II resemble somewhat to those of chromium, but less basic and more strongly hydrolysed because of smaller cationic radii,(but they are far stable than Cr(ii) compounds). Out of these three elements, only iron gives the characteristic simple(ie,aquated) tripositive ion. Cobalt(iii) gives large variety of co-ordination compounds, but that it is not a stable oxidation state in simple cobalt compounds is shown by the half reaction.[1,2]

$$Co^{2-}\ (aq) \rightleftharpoons Co^{3-}\ (aq) - (e) \qquad E_o = -1.842 \text{ volts}$$

Such a large negative value for the potential of the couple indicate that simple Co(iii) ion is capable of amidising not only many common ions, but water as well.[3] However, in presence many co-ordinating groups Co(iii) compounds are often formed at the expense of Co(ii) compounds. The co-ordination number of Co(iii) is 6, and ions or molecules in the co-ordination sphere are held with remarkable firmness, viz, chloride in such a position is not precipitated by silver ions.

The extent to which oxidation state can be stabilised due to

formation of complex or difficultly soluble complex may be measured in terms of the magnitudes of appropriate oxidation potentials. Some of the values[3] for various systems Co^{0}-Co(ii) and Co(ii) Co(iii) are summarised in the following table.

TABLE CCXIX

Couple	Half-reaction	E^{o}, volts
Co(o) - Co(ii)	$Co + xH_2O \rightleftharpoons Co^{2+}(aq) - 2e^-$	0.277
	$Co + 6NH_3(aq) \rightleftharpoons Co(NH_3)_6^{2-} - 2e^-$	0.422
	$Co + CO_3^{-2} \rightleftharpoons CoCO + 2e^-$	0.632
	$Co + 2OH \rightleftharpoons Co(OH)_2 + 2e^-$	0.73
	$Co + S \rightleftharpoons CoS(B) + 2e^-$	1.07
Co(ii)-Co(iii)	$Co^{2-}(aq) \rightleftharpoons Co^{3-}(aq) + e^-$	-1.842
	$Co(OH)_2 - OH^- \rightleftharpoons Co(OH)_3 + e^-$	-0.2
	$[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_6]^{3-} + e^-$	-0.1
	$[Co(CN)_6]^{4-} \rightleftharpoons [Co(Cn)_6]^{3-} + e^-$	0.83

The data summarised in the foregoing table indicate clearly that the oxidation of Co(o) to Co(ii) is much easier to effect in presence of precipitating or complexing agents than in their absence. These differences are even more striking with Co(ii)-Co(iii) couples. Addition of either hydroxyl ions or ammonia so reduces the oxidation power of Co (iii) that oxidation to the tripositive state may be effected with atmospheric oxygen (since $H_2O \rightleftharpoons 2H^+ + \frac{1}{2}O_2 + 2e^-$ $E_o = 1.229$ v

In presance of cyanide stabilisation is so pronounced that Co(iii) compound is oxidised by water and its stable existance in aquous solution is quite doubtful.

Amongst the three cyano complexes of cobalt, at least one has been extensively studied. viz., potassium cyano-cobalt (iii) ate, but comparatively very little work seems to have been done on Co(i) and Co(ii) cyano-complexes. Hence it was thought worthwhile to take up the study of some physico-chemical aspects of cyano-cobalt(II)ate, specially regarding its stability and electrometric behaviours. If successful, it might lead to the use of this compound as an analytical reagent of importance, this appearing probable on account of its high positive potential.

The study of potassium cyano-cobalt(II)ate is intresting from different angles. Not only this compound has got a controversial chemical formula and is difficult to obtain in a fairly stable and pure state, the compound shows varigated behaviour in some of its properties like stability, redox potential, complex formation with metal ions etc. A brief survey of the work done so far on this complex is given below.

Potassium cyanocobatate(II) was, for the first time, prepared by A. Descomp[4] in 1879 by adding a cold solution whereby he obtained a reddish brown precipitate. This precipitate was kept carefully at 0^{o} and was dissolved in excess KCN. The solution was then diluted with alcohol and amethyst coloured crystals were obtained on keeping (at 0^{o}) The properties of the complex were studied by Manchot and Herzoy[5]. They found that a solution of potassium cobaltacyanide is rapidly oxidised with oxygen and that its solution in KCN is fairly stable.

Electrochemical studies on this compound were taken up in 1926 by G. Grude [6]. He prepared the cobalt(II) compound by the electolytic reduction of potassium cyanocobaltate(III) in an alkaline solution, using 0.5M KOH and a slat concentration of o.1 M with current density 0.0133 amp/sq.cm. at a temp. of 12 . The deep brown solution so obtained was found to have a redox potential 0.821 volt. for Co(III) ratio of 0.086:0.014 moles while for a molar ratio of Co(II) to Co(I) as 0.0344:0.0656 the observed potential was 0.857.

The molecular formula of the complex still remains a problem of dispute to this day. L.SZego and P.Ostinelli[7] found it to be diamagnetic inspite of the odd number of electrons in the central atom which gives to magnetic spin proving thereby that it has got a molecular formula $K_4Co(CN)_6$. On the other hand Mondain Monval and Paris[8] while carrying out thermometric titrations of cobalt sulphate against potassium cyanide, found that the molecular formula should be $K_3Co(CN)_6$ On the basis of polarographic studies, Guido Sartori[9] gave the decomposition potential of $CoCl_2$ and KCN solutions as -0.690 and the probable complex was found to have the formula $K_4Co(CN)_6$.

More recently investigations on this complex have been carried out by potentiometric, polarographic and radiochemical methods. Treadwell and Dora Huber[10] in 1943, obtained potassium cyano-cobaltate(I complex gave both the biovalent and triovalent compounds with potassium ferrocyanide. The formation of $K_4Co(CN)_6$ has been reported in 1947 by Massakira Iguchi[11]. When cobalt chloride and potassium cyanide are mixed in the atmosphere of hydrogen gas, it was observed that the gas was absorbed and the adsorption was accelerated in the presence of KCl, NaCl, NaBr, and $NaNO_3$.

Amongst the other workers in support of the formation of cyano-cobaltate(II), mention may be made of R.Peters[17], T.M.Lowery,[18] N.V.Emelianova,[19] and G.Sastori[20] while experinental evidence of E E.Ruppond Pfeiffing,[21] P.Edelmann,[22] E.Miller and W.Schiillig[23] and G. Glasstone and Speakman[24], go in support of a pentacyanide.

Thermometric titrations of cobalt nitrate and potassium cyanide were done by J.Crempux and Mondain Monval[25] and they obtained three breaks in dilute solutions corresponding to the formation of $Co(CN)_2$, $K_2Co(CN)_4$ and $K_4Co(CN)_6$. It is less stable in concentrated solutions than in dilute solutions. Hume and Kolthoff[26] carried out studies on the reduction of Cobalt (III) complex and Co(I) and Co(II) complexes and calculated the redox potential of Co(II) Co(III) and compared with the accepted values. According to them the value hither to known could not be considered valid.

A systematic study of the nature of the complex formed between Co(ii) and KCN and its exchange with radio cyanide was taken up by Ademson[27] in 1951. He prepared the solid complex by adding cooled concentrated solution of KCN to cooled 0.2 N Co(ii) nitrate in an atmosphere of nitrogen, The mixture was slowly chilled and precipitated by 80 % alcohol. A mass of thin violet platelets was obtained which was filtered rapidly and was finally dried in a vacuum desicator after washing with 80 % alcohol. Analysis of this complex by ion exchange method led him to the following conclusions:-

(i). There is at present no conclusive evidence for the existence of hexa cyano cobaltate(II) complex either as solid, or as a reasonably stable species in solution. The most stable cyanide complex contains five cyanides per cobalt and is Co-valently bonded. The information

presently available does not distinguish between the two most likely structures for the penta cyanide in solution, normely, hexa co-ordinated $Co(H_2O.Cy_5)^{3-}$ and penta co-ordinated $Co(CN)_5^{3-}$ ion.

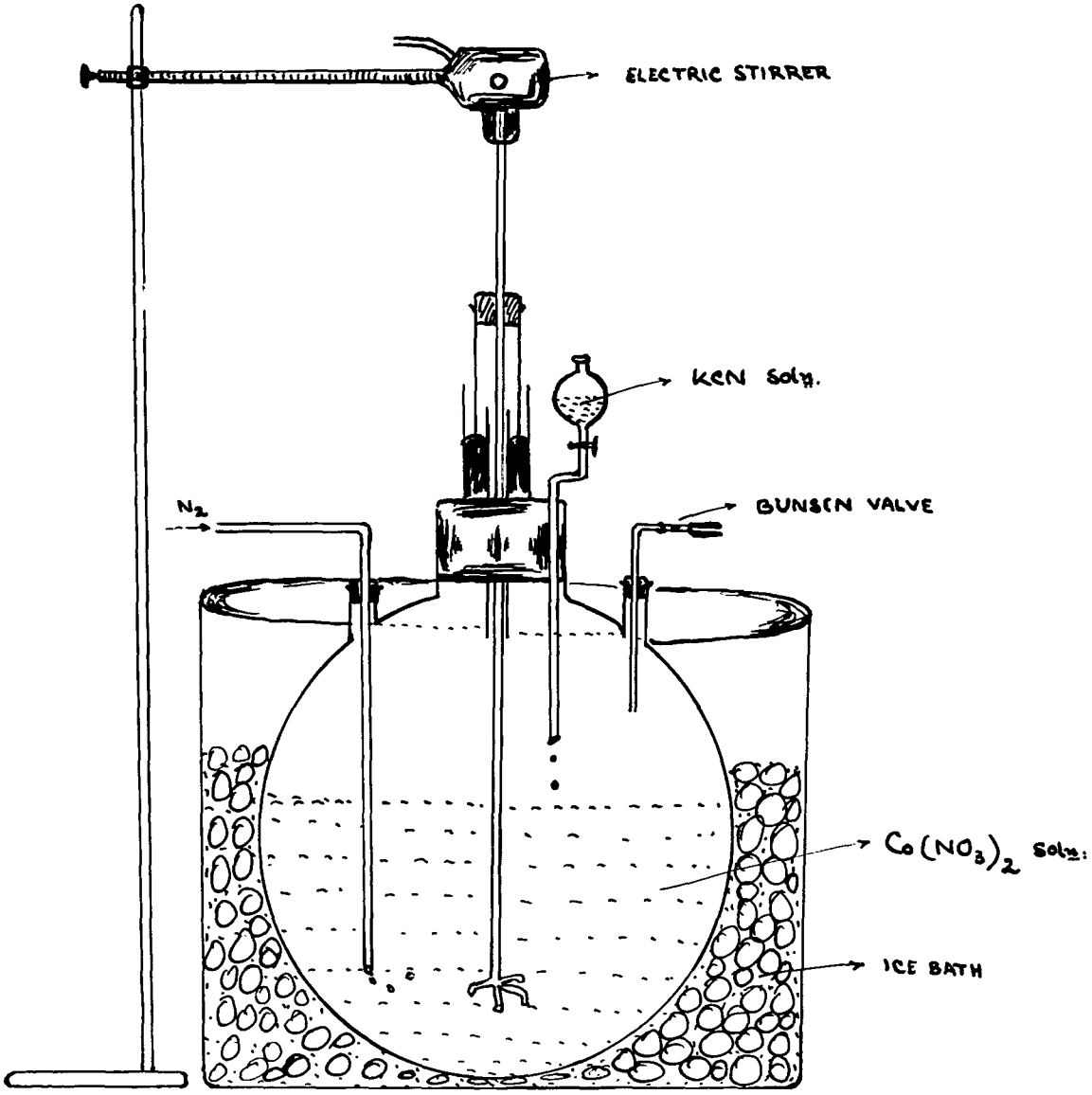
Heiber and Bortenstein[28] obtained a new compound $K_4Co(CN)_4$ when the blue alcoholic solution of potassium decolourised by adding pulverised K_3CoCy_6 . This brown violet crystalline substance decomposes water with the evolution of hydrogen and is attacked by dry carbon dioxide. Smith and co-workers[29] studied the oxidation product having the composition $K_3Co(CN)_6$ (assuming the formula of potassium cyano-cobaltate(II) as K_3CoCy_5). They obtained a diamagnetic product.having the composition $K_3CoCy_5(OH)$ OH. On the basis of titration curves and spectrophotometric data, they conclude that during oxidation $CoCy_4(OH)_2^{---}$ and $CoCy_6^{---}$ are found in early stages.

From the above, it is evident that although sufficient data are available on the properties of this complex, much is still wanting as far as the problem of the composition and its electro-chemical behaviour is concerned. It appears as if a systematic approach on these fundamental aspects has never been made. The present work is a partial attempt in this direction and specially deals with the electrometric studies on the compounds.

EXPERIMENTAL

The method recommended by Smith and co-workers[29] with slight modification was followed for the preparation of the complex. 60 gm. of hydrated cobalt nitrate $Co(NO_3)_2.6H_2O$, was dissolved in about 150 c.c. of air free distilled water in three necked flask of 1000 cc.

FIG. 8


ELECTRIC STIRRER
KCN Soln.
N_2
BUNSEN VALVE
$Co(NO_3)_2$ Soln.
ICE BATH

capacity. The solution was chilled in an ice bath and the air in the flask was completely expelled by a current of purified nitrogen(Fig 8). An ice cold saturated solution of KCN was then added dropwise(from the dropping funnel) until the precipitate which was first formed had redissolved. (The whole mixture was kept stirring by an electric stirrer). To the resulting olive green solution maintained at 0^{o}, cooled 95% alcohol(about 500 c.c.) was added slowly and the whole mixture kept aside for about four hours when copious precipitate of violet crystals was formed. The current of nitrogen was maintained throughout the experiment. The precipitate was quickly collected on a sintered glass filter(in nitrogen atmosphere), washed several times with cooled 95% alcohol and dried in a vacuum dessicator over anhydrous $CaCl_2$. (The dessicator filled with nitrogen was repeatedly evacuated). The dry sample was preserved in the dessicator itself.

Chemical analysis of the complex:

The complex dried in the vacuum dessicator was analysed for Co, K and nitrogen. The acid digestion method was followed for breaking the complex. A weighted quantity of the complex(the weighing was done in minimum time with minimum exposure to air) was taken in a round bottomed flask of 250 c.c. capacity and about 25 c.c. of concentrated sulphuric acid added to it. The contents were kept briskly boiling for about half an hour and then heated to complete dryness to remove the cyanogen. The mass was then dissolved in minimum quantity of dilute sulphuric acid and made up to 250 c.c. in a measuring flask This solution was used for the estimation of cobalt and potassium.

Estimation of Cobalt:

The cobalt content in the complex was estimated volumetricall by potassium cobaltinitrite method.[30] The principle of the method

is that cobalt is precipitated as potassium cobaltinitrite $2K_3Co(NO_2)_3 .3 H_2O$ from a solution made slightly acidic with acetic acid, by the addition of a hot solution of potssium nitrite. The precipitate was then decomposed with known excess of potassium permanganate and the unused permanganate back estimation.

40.0 c.c. of the cobalt sulphate solution was pipetted out from the 250 c.c. flask into a beaker and neutralised by gradual addition of a 10 % solution of potassium carbonate. 2.0 to 3.0 c.c. of acetic acid was then added to it and boiled. 15 to 20 gm. of potassium nitrite dissolved in 25 c.c. of water and acidified with 2 c.c. of acetic acid was then heated to boiling and this hot solution was added to the cobalt solution with brisk stirring. The contents of the beaker was kept boiling for half an hours and then allowed to stand for about six hours. It was then filtered through a fresh Gooch Crucible and washed with a 10% solution of potassium acetate .

The precipitate was then transferred to a beaker (along with the asbestos) and 20 c.c. of 4 N sulphuric acid and 20 c.c. of N potassium permanganate added to it. About 1.0 gm. of solid potassium iodide was then added to the mixture stirred 5 minutes and the liberated iodine was titrated against standard sodium thiosulphate using starch as indicator. The experiment was done in duplicate.

Estimation of Potassium and Cyanogen:

Potassium and cyanogen were estimated by the methods described earlier (vide part I page 190) and quite reproducible results were obtained.

Estimation of water content.

The deviation of the total percentage of Co, A and $C\tilde{N}$ from 100, was taken to be due to water.

The results of the analysis are tabulated as below:

TABLE CCXX

Percentage Constituents.

Expt. No	% K	% Co	% CN	Total	water %
1	36.72	17.95	39.61	-	-
2	36.60	17.67	40.48	-	-
Average	36.66	17.81	40.05	94.52	5.48

TABLE CCXXI

Calculation of the empirical formula of the complex.

Constituents		Percentage	Equivalent	Ratio
1	Co	17.81	0.3021	1.0
2	K	36.66	0.9376	3.103
3	CN	40.05	1.540	5.098
4	H_2O	5.48	0.3045	1.008

The empirical formula of the complex thus found to be $K_{3.103}\ Co_1(CN)_{5.098}\ H_2O_{1.008}$ which may be written as $K_3[Co(CN)_5.H_2O].0.1KCN$. This shows that the complex is having the composition $K_3[Co(CN)_5H_2O]$ and it contains about 0.1 mole KCN adsorbed per mole of the complex. This much adsorption of the complex was expected since it was from a solution containg excess of KCN and was washed with 80 % of alcohol(not water). The empirical formula weight of the complex =330.7

The equivalent weight of the complex was determined as follows:

20.0 c.c. of 0.1 N $K_3Fe(CN)_6$ was taken in a flask and 5 c.c. of 0.1 N potassium cyanide added to it. 0.3307 gm. of the complex was

TABLE CCXXII

Concentration of cobaltnitrate	= 5 m.molar.
Concentration of gelatine	= 0.005 %
Concentration of potassium chloride	= 1 M
Drop time (at 1 volt)	= 3.2 sec.
Temperature	= 5°

Applied e.m.f.	Galv. readings (in m.m.)	Applied e.m.f.	Galv.readings (in m.m.)
0.0	-1.0	1.4	25.0
0.1	-0.5	1.6	26.0
0.2	-0.0	1.7	27.0
0.8	-0.5	1.8	27.75
1.0	1.75	1.9	30.0
1.1	10.75	2.0	96.0
1.15	19.0		
1.2	23.0	(Vide curve No. 184)	
1.3	25.0		

The half wave potential for the reduction of Co(II) under under these conditons was found to be -1.12 volt(vide curve No. 184) as against -1.2 volt reported by Lingane and Kerlinger.[32]

Titrations were carried out taking different concentrations of cobalt nitrate in the cell and adding KCN solution with the help of an automatic microburette. All the solutions were prepared from reagent grade chemicals and in air free double distilled water. The supporting electrolyte, gelatin and cobatnitrate solution, were taken in the titration cell kept in an ice bath (temperature maintained at 2-3).Complete dearation was effected by acurrent of purified nitrogen and maximum precaution was taken to prevent the solution from coming into contact with air. A potential of -1.25 was then applied and increasing amounts of KCN solution added noting the galvanometer readings two minutes after eacg addition, and through

then added to the above. The complex reduced the ferrocyanide and the latter was estimated by the method of Miller and Diefenthaler.[31] About 270gm. each of zinc sulphate and potassium iodide were added and the free iodine titrated against 0.1 N sodium thiosulphate using starch as indicator.

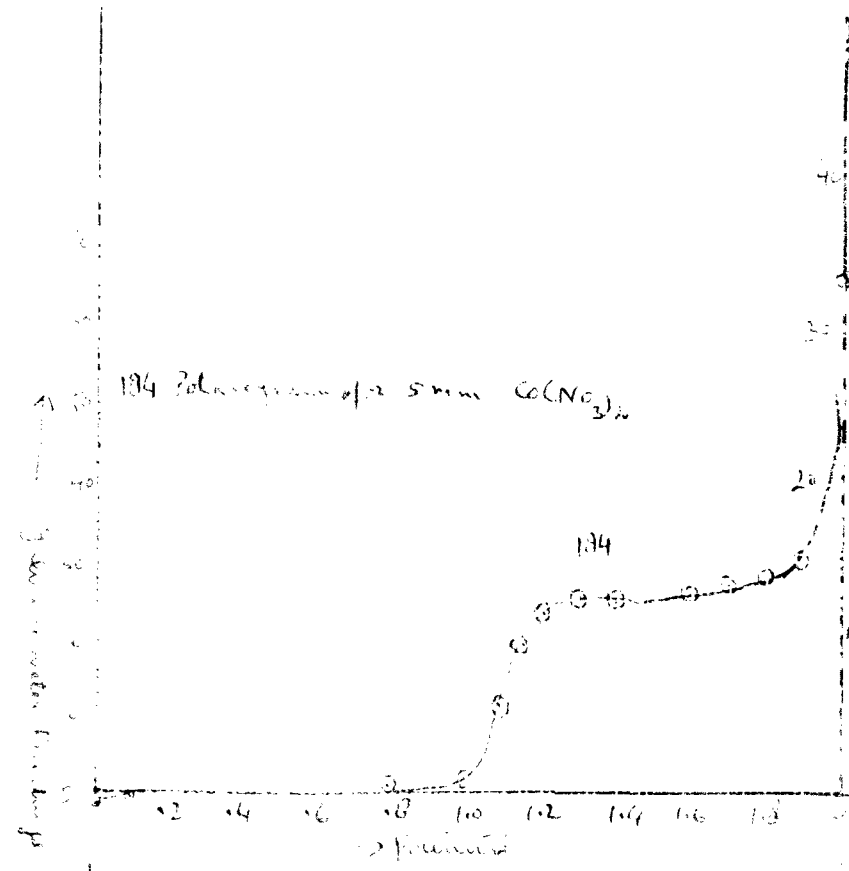
Volume of 0.1 N potassium ferrocyanide	= 20.0 c.c.
Volume of 0.1 N thiosulphate(titre value)	= 9.75 c.c.
∴ Volume of thiosulphate equivalent to the ferrocyanide used up by the complex	=20-9.75 = 10.25 c.c.
∴ Normality of the complex solution weight of the complex in the solution(25 c.c.)	= $\frac{10.25 \times .1}{25}$ = 0.3307
∴ gm./litre of the complex	= 13.228 gm.
.. Equivalent weight of the complex	= $\frac{13.228 \times 25}{0.1 \times 10.25}$ = 322.5

This value is almost in agreement with the empirical formula weight (330.7) calculated on the basis of chemical analysis.

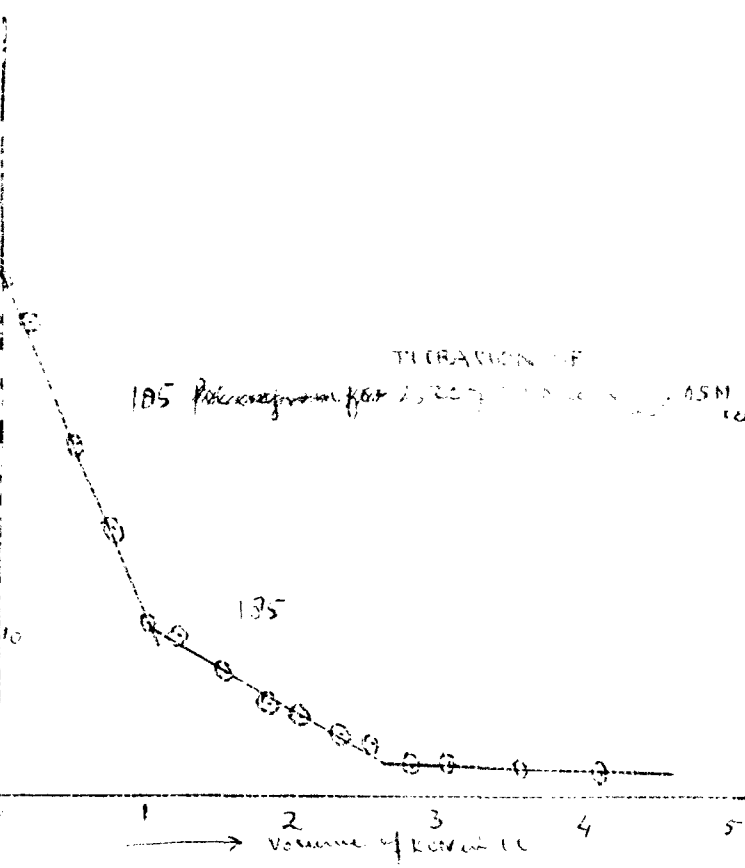
Composition of the complex by amperometric titration.

To confirm the conclusion from the chemical analysis amperometric titrations were carried out between cobalt nitrate and potassium cyanide at low temperature and out od contact of air. This apparatus and technique described earlier (vide Part I page 125) were used in these experiments.

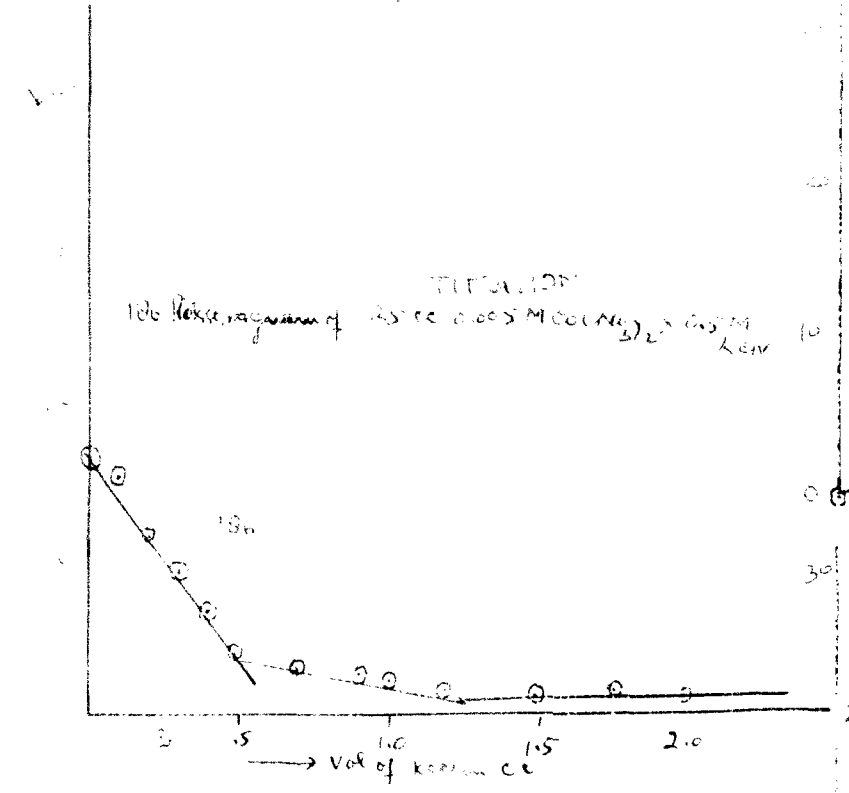
Fibstly a polarogram of cobalt(II) nitrate was taken in 1 N KCL as supporting electrolyte and 0.005 % gelatine as maximum suppressor. The readings are given on the next page.



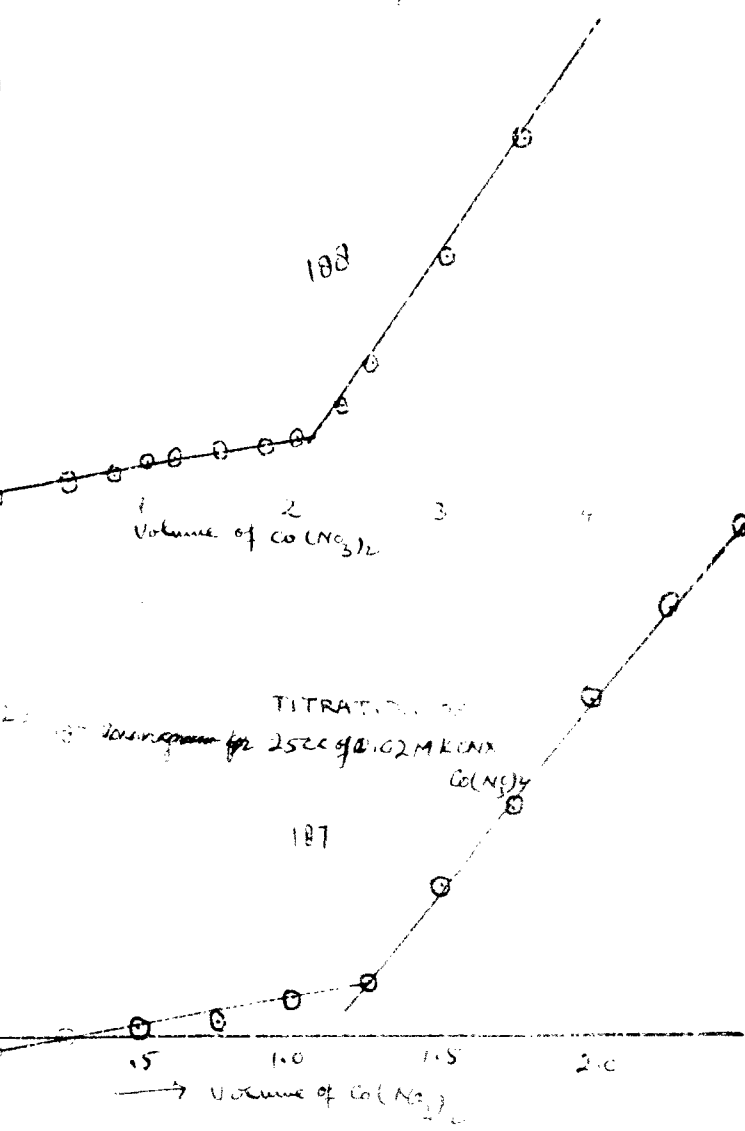
184 Potentiogram of 25 ml $Co(NO_3)_2$



185 Potentiogram for 25cc of [illegible] 0.5M



186 Potentiogram of 25 cc 0.05 M $Co(NO_3)_2$ vs 0.05 M KCNS



TITRATION OF

187 Potentiogram for 25cc of 0.02 M KCNS

mixing by the current of nitrogen. Some of the readings for direct and reverse titrations are tabulated as follows:

A concentration of 0.005 % gelatin was used in every case Temperature 2 to 3° , drop time 3.1 sec. and sensitivity of the apparatus 5 X

(a) Direct titrations $Co(NO_3)_2$ in the cell.

TABLE CCXXIII

Volume of 0.1 N $Co(NO_3)_2$ = 2.5 c.c.
Total Vol. made up = 25 c.c.
Strength of $Co(NO_3)_2$ = 0.01 M
Strength of KCl = 0,5 M
Strength of KCN = 0.5 M

Vol. of KCN	Galv. readings (in m.m.)
0.0 c.c.	33.0
0.2 "	30.5
0.5 "	22.5
0.75 "	17.0
1.0 "	11.0
1.2 "	10.25
1.5 "	8.0
1.8 "	6.0
2.0 "	5.0
2.3 "	4.0
2.5 "	3.25
2.75 "	2.0
3.0 "	2.0
3.5 "	1.75
4.0 "	1.5

(Vide curve No. 185)

At the second break
25 c.c. 0,01 M $Co(NO_3)_2$ = 2.55 c.c. of 0.5 M KCN

= 127.5 c.c. of 0.01 M KCN

TABLE CCXXIV

Volume of 0.1 M $Co(NO_3)_2$ = 1.25 cc
Total Vol.made up = 25 c.c.
Strength of $Co(NO_3)_2$ = 0.005 M
Strength of KCl = 0.5 M
Strength of KCN = 0.5 M

Vol. of KCN	Galv. readings (in m.m.)
0.0 c.c.	16.0
0.1 "	15.0
0.2 "	11.5
0.3 "	9.0
0.4 "	6.5
0.5 "	3.75
0.7 "	3.0
0.9 "	2.5
1.0 "	2.25
1.2 "	1.5
1.4 "	1.75
1.5 "	1.5
1.75 "	1.5
2.0 "	1.25

'Vide curve No. 186)

At the second break,
25 c.c. 0.005 M $Co(NO_3)_2$
= 1.25 c.c. of 0.5 M KCN

= 125 c.c. 0.005 M KCN

(b) Reverse titrations-KCN in the cell

TABLE CCXXV

Vol. of 0.1 KCN = 5 c.c.
Total volume = 25 c.c.
Concentration of KCN = 0.02 M
Strength of $Co(NO_3)_2$ = 0.1 M
Concentration of KCl = 0.5 M

Vol of $Co(NO_3)_2$	Galv. readings (in m.m.)
0.0 c.c.	-0.5
0.2 "	0.0
0.4 "	0.5
0.6 "	1.0
0.8 "	2.5
1.0 "	3.5
1.2 "	9.5
1.4 "	14.25
1.6 "	21.0
1.8 "	27.0
2.0 "	32.5

(Vide curve No. 187)

25 c.c. 0.02 M KCN
= 1.0 c.c. 0.1 M $Co(NO_3)_2$
= 5 c.c. 0.02 M $Co(NO_3)_2$

TABLE CCXXVI

Vol. of 0.1 M KCN = 10 c.c.
Total volume = 25 c.c.
Concentration of KCN = 0.04 M
Strength of $Co(NO_3)_2$ = 0.1 M
Concentration of KCl = 0.5 M

Vol. of $Co(NO_3)_2$	Galv. readings (in m.m.)
0.0 c.c.	-1.0
0.5 "	0.0
0.8 "	0.5
1.0 "	1.25
1.2 "	1.5
1.5 "	2.0
1.8 "	2.25
2.0 "	2.75
2.3 "	5.0
2.6 "	7.75
3.0 "	14.5
3.5 "	22.0

(Vide curve No. 188)

25 c.c. 0.04 M KCN
= 2.1 c.c. 0.1 M $Co(NO_3)_2$
= 5.25 c.c. 0.04 M $Co(NO_3)_2$

In the case of direct titrations where KCN was added to cobalt nitrate solution, two breaks were obtained (vide curve 185 and 186), the first due to formation of $Co(CN)_2$ and the second when 5 equivalents of KCN were added. At the latter point the solution became quite clear. In the case of reverse titration there was appearence of slight turbidity with simoultaneous rise in the current. The following inferences could be drawn from the amperometric titrations between cobaltnitrate and potassium cyanide solution.

(i) By the addition of potassium cyanide to cobaltnitrate a sparingly soubbe precipitate is formed.

(ii) This precipitate dissolves in excess KCN to give the souble complex when 5 equivalence of KCN have been added.

(iii) This complex is not reduced at the dropping mercury electrode at the potential of -1.25 volts.

(iv) Reverse titrations also show the formation of the complex with $Co(NO_3)_2$:KCN as 1:5 (Vide tables 228 and 229); 25 c.c. of KCN = 5 and 5.25 c.c. $Co(NO_3)_2$ respectively with concentrations 0.2 M and o.o4 M)

<u>The anodic wave of the pentacyano complex:-</u>

Since the aquous solution of the Co(ii) complex is very unstable and is liable to instantaneous oxidation, the following method was employed. The solutions obtained in the cell after the direct titration were directly used to for the study of the nature of the anodic and cathodic wave for the complex. The readings are tabulated on the next page, the conditions being the same as for in tables 233 and 234.

TABLE CCXXVII

(readings for solution under table ccxxiii)

Potagainst s.c.e.	Galv.readings (in m.m.)
0.0 volt	-40.0
0.05 "	-39.0
0.1 "	-37.5
0.2 "	-34.5
0.3 "	-25.0
0.4 "	-10.0
0.5 "	-2.25
0.6 "	-0.5
1.0 "	0.0
1.1 "	0.5
1.2 "	1.5
1.3 "	3.5
1.4 "	4.5
1.7 "	4.5
1.8 "	5.0
1.9 "	16.5
2.0 "	36.0

(Vide curve No. 189)

TABLE CCXXVIII

(Readings for solution under table ccxxiv)

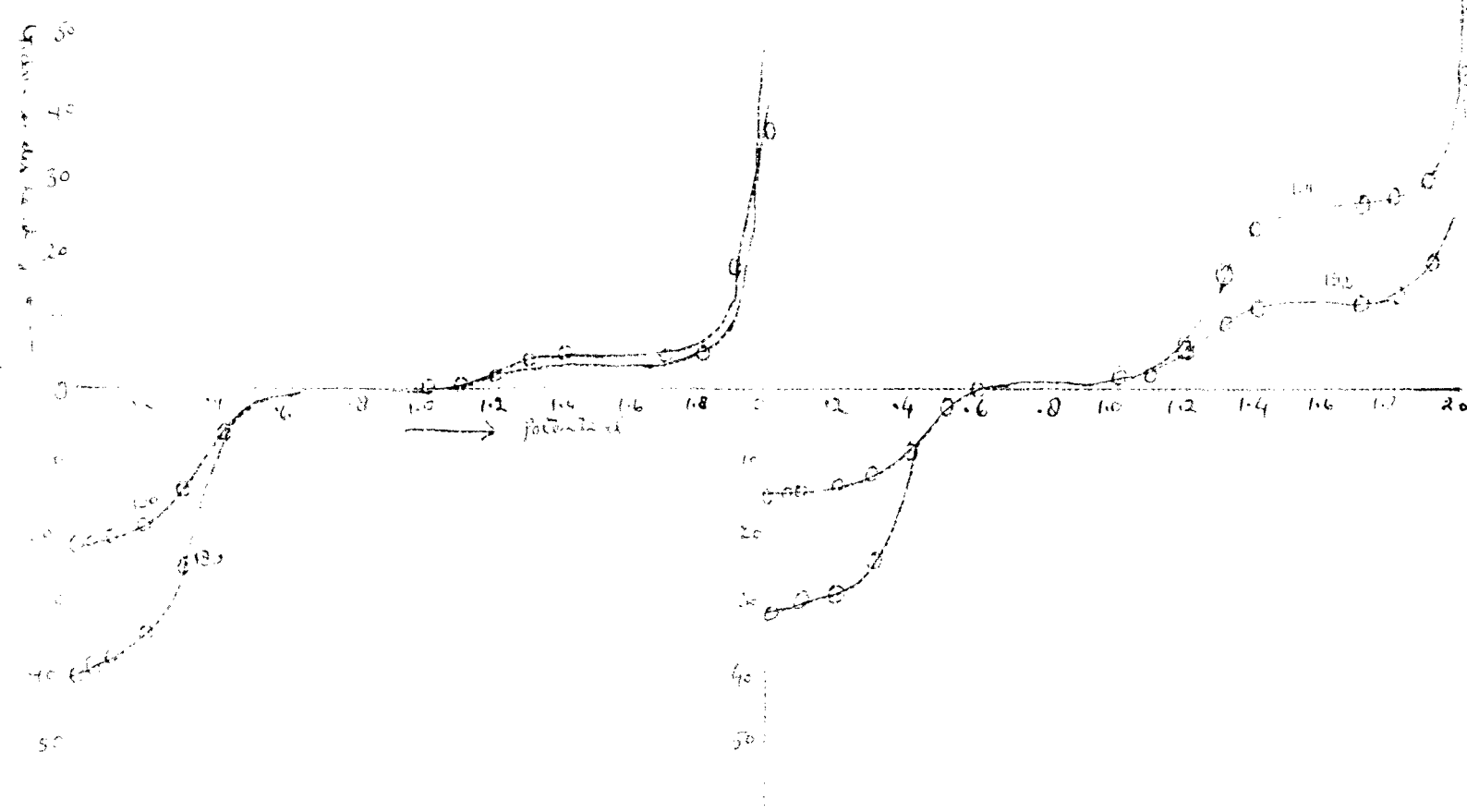
Pot. against s.c.e.	Galv. readings (in m.m.)
0.0 volt	-22.0
0.05 "	-21.5
0.1 "	-21-0
0.2 "	-19.5
0.3 "	-14.5
0.4 "	-6.5
0.5 "	-1.25
0.6 "	-0.25
1.0 "	0.0
1.1 "	0.25
1.2 "	1.25
1.3 "	3.0
1.4 "	4.0
1.7 "	4.0
1.8 "	4.0
1.9 "	15.5
2.0 "	37.0

(Vide curve No. 190)

It is seen that the cyanide complex gives an irreversible anodic wave with a half wave potential of -0.35 volt. The cathodic part of the waves (curve 189 and 190) show that some of the solution had been oxidised in spite of all the precautions (and this may be due to water oxidation) and this oxidised product undergoes reduction at a potential of -1.3 volts, under these conditions. In order to varify this part of the wave, readings were taken after oxidising part of the complex by the addition of hydrogen per-oxide (0.1 N). The latter was selected as oxidising agent in order to avoid the presenceof undesireable product in the test solution. Two polarograms were taken with different extent of oxidised product and the readings are tabulated as follows:- The solutions under ... data table ccxxiii and ccxxvii were used. Drop time, temp. etc were kept the same as in other experiments:

POLAROGRAMS OF PENTA CYANOCOBALTATE

CURVES I & II



[illegible]	[illegible]
Volume of 0.1 M H_2O added = 0.5 c.c.	Volume of 0.1 M H_2O added 0.5 c.c.

Pot. against S.C.E.	Galv. readings (in m.m.)	Pot. against S.C.E.	Galv. readings (in m.m.)
0.0 volt	-31.5	0.0 volt	-[illegible].0
0.05 "	-29.5	0.05 "	-[illegible].5
0.1 "	-28.0	0.1 "	-[illegible].5
0.2 "	-26.0	0.2 "	-[illegible].5
0.3 "	-24.5	0.3 "	-[illegible].0
0.4 "	-10.25	0.4 "	- 5.0
0.5 "	- 2.5	0.5 "	- 2.0
0.6 "	0.0	0.6 "	0.25
0.0 "	1.0	1.0 "	1.5
1.1 "	1.5	1.1 "	2.0
1.2 "	4.75	1.2 "	5.0
1.3 "	9.5	1.3 "	10.25
1.4 "	11.0	1.4 "	[illegible].5
1.7 "	12.0	1.7 "	23.5
1.8 "	13.0	1.8 "	26.5
1.9 "	18.0	1.9 "	28.0
2.0 "	42.5	2.0 "	52.0

(Vide curve No. 191)

Anodic half wave pot. = -0.23 V
Cathodic half wave poten -1.35 V.

(Vide curve No. 192)

Anodic half wave pot. = 0.40 V
Cathodic half wave pot. = 1.25 V

In order to study the identity of the product obtained by the oxidation of cyanocobaltatepolarogram for hydrono-pentacyano-cobalt(III) were obtained. The compound was prepared by the method of Smith and co-workers[29] by drawing air through pentacyanocobalt(II) till the oxidation was complete. The brown solid product thus obtained was washed with alcohol and then with ether and dried in a vacuum dessicator over concentrated sulphuric acid. Each molar solution of the complex (accepting the formula as $K_3[Co(CN)_5CN]\cdot H_2O$ as proposed by the above authors) was prepared in air free distilled water and polarogram taken with KCl and KCN as supporting electrolytes. The temperature conditions, droptime, concentration of the maximum suppressor etc. were maintained the same as in the previous experi-

TABLE CCXXXI

Conc. of complex = 5 m.mole
Conc. of KCl = 0.5 M
Sensitivity = 2 X

Pot. against s.c.e.	Galv. readings (in m.m.)
0.0	-1.5
0.1	0.0
0.5	0.0
0.8	0.0
0.9	1.0
1.0	3.0
1.1	6.5
1.2	12.0
1.3	18.0
1.35	22.0
1.4	29.0
1.5	38.0
1.6	41.0
1.7	41.0
1.8	41.0
1.9	41.0
1.95	43.0
2.0	83.0

(Vide curve No. 193)

Half wave potential = 1.32 Volt
Curve drawn out reduction irreversible

TABLE CCXXXII

Conc. of complex = 5 m.mole
Conc. of KCN = 0.5 M
Sensitivity = 2 X

Pot. against s.c.e.	Galv. readings (in m.m.)
0.0	-2.0
0.1	0.5
0.5	0.0
0.8	0.5
0.9	2.0
1.0	4.5
1.1	8.0
1.2	14.0
1.3	28.0
1.35	30.0
1.4	36.0
1.5	40.0
1.6	41.0
1.7	41.0
1.8	42.0
1.9	44.0
1.95	52.0
2.0	92.0

(Vide curve No. 194)

Half wave potential = -1.26 volt
Curve drawn out Reduction irreversible.

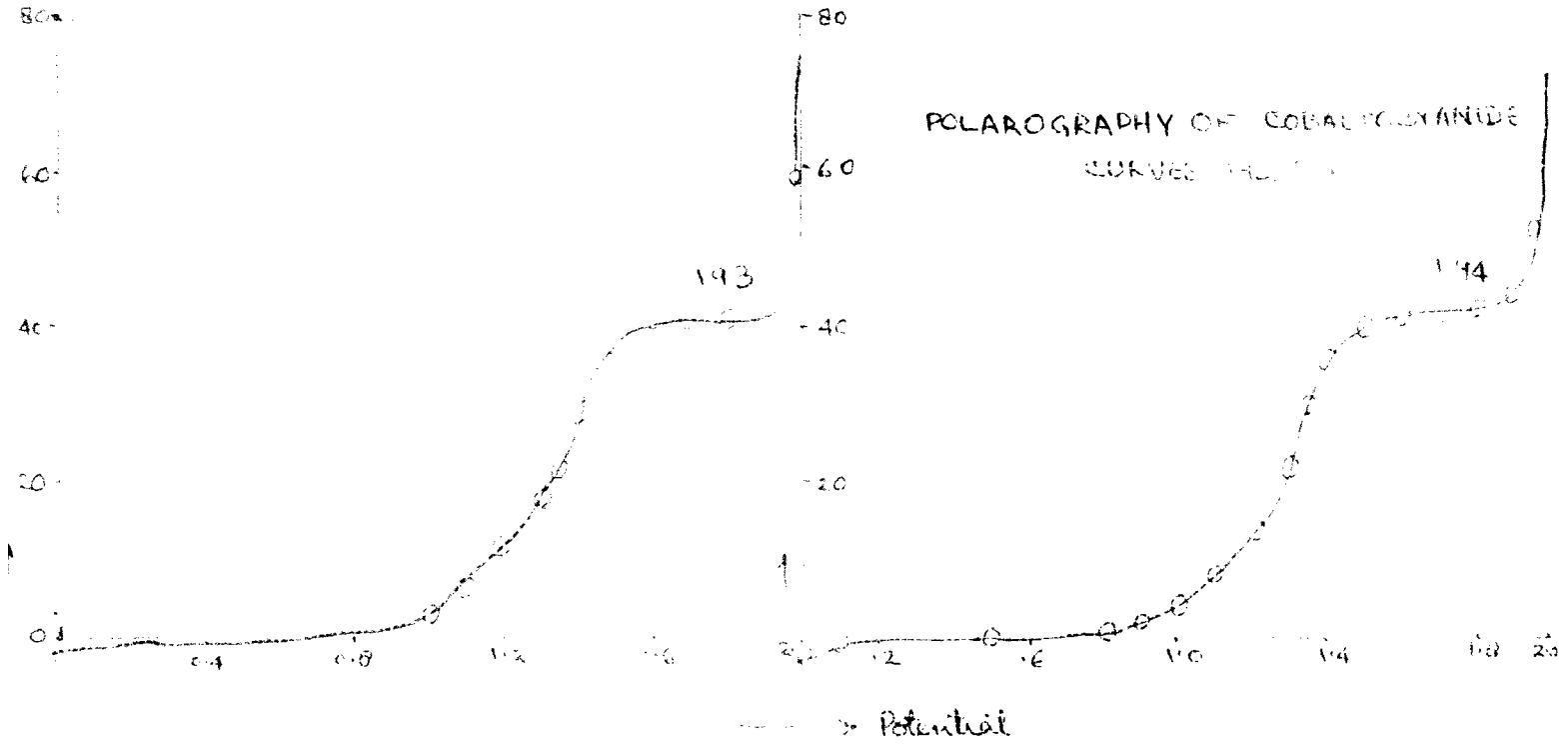
From tables ccxxix and ccxxx (curves 191, 192) it is seen that by the addition of hydrogen peroxide the pentacyanocobalt(ii) undergoes oxidation and the oxidised product is reducible at the dropping mercury electrode at a potential of -1.28 volts(-1.25 to -1.3 volts). Both these electrode reactions are quite irreversible as it could be seen from the nature of the curve (a large inflection at zero current). It is evidenfrom the polarograms of hydroxopentacyanocobaltate(iii) and of the oxidised product from cyanocobaltate(ii) that these compounds are identical and give the sema characteristic polarograms with the same half-wave potential.

4. POTENTIOMETRIC STUDIES:

Potentiometric titration between cobalt nitrate and potassium cyanide were carried cut, in order to confirm the observations on amperometric and analytical studies. The air tight cell described earlier (page 24) in conjunction with a smooth platinum and calomel electrodes, was used for the titrations. Purified nitrogen was used for deaeration and maintaining an inert atmosphere. The current of nitrogen also served as an efficient stirrer during the experiment. All the titrations were carried out at a temperature $2 \pm 0.5^{\circ}$ C by keeping the cell in an ice bath.

Standard solutions of cobalt(ii) nitrate and potassium cyanide were prepared from A.R. samples of the reagents and their strengths determined. (KCN was standardised against silver nitrate and cobalt by cobaltinitrite method).

A known quantity of cobalt nitrate was taken in the cell and the current of nitrogen passed through it for about half-an-hour for complete replacement of air. Aliquots of standard potassium cyanide solution were then added with the help of an automatic microburette, noting the potential after stirring and waiting for about five minutes after each addition. The readings are tabulated on the next page.


POLAROGRAPHY OF COBALTICYANIDE
CURVES
193
194
Potential

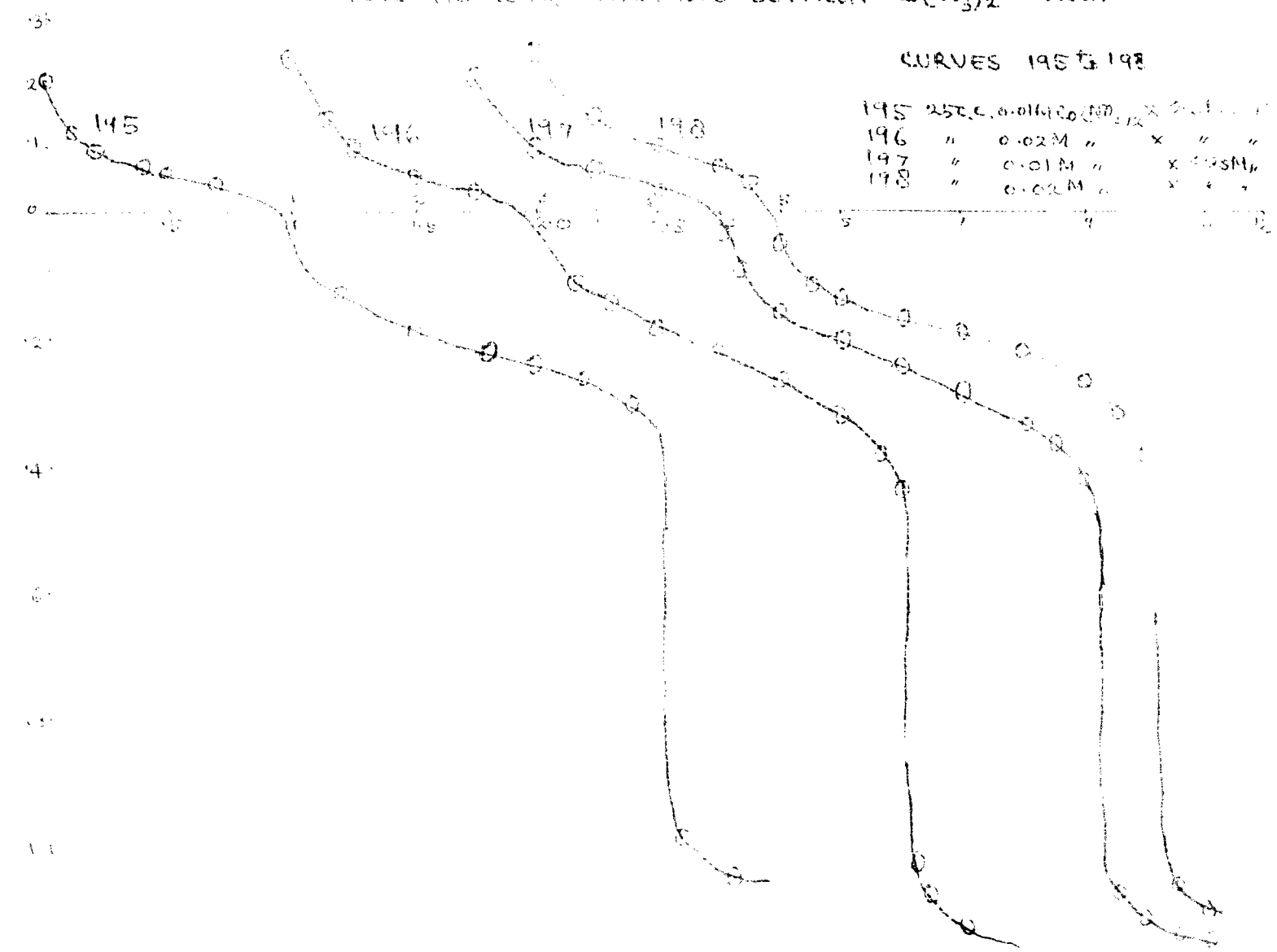

TITRATIONS BETWEEN $Co(NO_3)_2$ and KCN
CURVES 195 to 198
195 25 c.c. 0·01M $Co(NO_3)_2$ x c.c. N/10 KCN
196 " 0·02M " x " "
197 " 0·01M " x 0·05M "
198 " 0·02M " x " "
195
196
197
198

TABLE CCXXXIII

Vol. of 0.1 M $Co(NO_3)_2$ = 2.5 c.c.

Volume made up. = 25 c.c.

Concentration of KCN = 0.5 M

Vol. of KCN	Pot. against s.c.e.
0.0 c.c.	-0.210
0.1 "	-0.125
0.2 "	-0.090
0.4 "	-0.075
0.5 "	-0.060
0.7 "	-0.040
1.0 "	0.030
1.2 "	0.135
1.5 "	0.190
1.8 "	0.225
2.0 "	0.240
2.2 "	0.275
2.4 "	0.275
2.5 "	0.365
2.6 "	0.970
2.8 "	1.035

(Vide curve No. 195)

25 c.c. 0.01 M $Co(NO_3)_2$

= 2.525 c.c. 0.5 M KCN

= 127.3 c.c. 0.01 M KCN

TABLE CCXXXIV

Vol. of 0.1 M $Co(NO_3)_2$ = 5.0 c.c.

Vol. made up = 25 c.c.c

Concentration of KCN = 0.5 M

Vol. of KCN	Pot. against s.c.e.
0.0 c.c.	-0.24
0.25 "	-0.145
0.5 "	-0.095
1.0 "	-0.050
1.5 "	-0.030
2.0 "	0.025
2.3 "	0.115
2.6 "	0.360
3.0 "	0.190
3.5 "	0.225
4.0 "	0.270
4.5 "	0.325
4.8 "	0.385
5.0 "	0.440
5.1 "	1.010
5.2 "	1.065
5.5 "	1.100
6.0 "	1.140

(Vide curve No. 196)

25 c.c. 0.02 M $Co(NO_3)_2$

= 5.05 c.c. 0.5 M KCN

= 126.3 c.c. 0.02 M KCN.

TABLE CCXXXV

Vol. of 0.1 M $Co(NO_3)_2$ = 2.5 c.c.
Total volume made up = 25 c.c.
∴ Conc of $Co(NO_3)_2$ = 0.01 M
∴ Conc. of KCN = 0.25 M

Vol. of KCN (in c.c.)	Pot. against s.c.e.
0.0	-0.205
0.5	-0.100
1.0	-0.065
1.5	-0.035
2.0	-0.030
2.5	-0.110
3.0	0.205
3.5	0.250
4.0	0.295
4.5	0.335
4.75	0.355
5.0	0.430
5.25	1.060
5.5.	1.100
5.75	1.130
6.0	1.155

(Vide curve No. 197)

25 c.c. 0.01 M $Co(NO_3)_2$
= 5.1 c.c. 0.25 M KCN
= 127.5 c.c. 0.01 M KCN

TABLE CCXXXVI

Vol. of 0.1 M $Co(NO_3)_2$ = 5.0 c.c
Total volume made up = 25 c.c.
∴ Conc. of $Co(NO_3)_2$ = 0.02 M
∴ Conc. of KCN = 0.25 M

Vol. of KCN (in c.c.)	Pot. against s.c.e.
0.0	-0.250
1.0	-0.145
2.0	-0.100
3.0	-0.075
3.5	-0.045
4.0	0.045
4.5	0.110
5.0	0.140
6.0	0.170
7.0	0.195
8.0	0.220
9.0	0.275
9.5	0.320
10.0	0.390
10.5	1.050
11.0	1.095

(Vide curve No. 198)

25 c.c. 0.02 M $Co(NO_3)_2$
= 10.15 c.c. 0.25 M KCN
= 126.9 c.c. 0.02 M KCN

From the potentiometric titration between cobalt(ii) nitrate and potassium cyanide it is seen that two distinct breaks are obtained (vide curves 195 to 198). The first break occurs after the addition of 2 equivalents of KCN and is due to the formation of the precipitate of $Co(CN)_2$. On further addition of KCN, the precipitate starts dissolving and after the addition of about five equivalents of the reagents the precipitate completely disappears accompanied by a sharp break in potential. The results for the second break are summarised on the next page.

TABLE CCXXXVII

Strength of $Co(NO_3)_2$	Vol. of $Co(NO_3)_2$	Strength of KCN	Volume of KCN in the same molar conc.
0.01 M	25 c.c.	0.5 M	127.3 c.c.
0.02 M	25 c.c.	0.5 M	126.3 c.c.
0.01 M	25 c.c.	0.25 M	127.5 c.c.
0.02 M	25 c.c.	0.25 M	126.9 c.c.

These results confirm that the complex formed is a penta-cyanide. No further breaks in the titration curves were observed on further addition of KCN. The slightly higher value for KCN (about 1.5 to 2 %) are probably due to the slow attainment of the equilibrium.

Potential changes of Cobalt(ii)-(iii) cyanide systen in presence of electrolytes.

The cyanocobaltate (ii) complex has been found to be so unstable in aqueous solutions that it decomposes water getting itself converted to cobaltate(iii) state. The extent to which this oxidation is promoted or suppressed by the presence of various foreign ions in solution, can be measured by the changes in oxidation reduction potential of the system.[27] At ordinary temperature, the oxidation of cyanocobalt (ii) in aqueous solution is so rapid and immeasurable, that these experiments were carried out at low temperatures 2 to 0.5 ^{o}C . The violet flasks of potassium pentacyano-cobaltate(ii) dissolves very readily in water giving a blood red solution which is soon converted to the brown hydroxo-penta-cyano-cobaltate(iii) and the latter gradually turns colourless due to slow formation of hexacyanocobaltate(iii)[27,29]

Variations in the electrode potential of penta cyano-cobaltate(ii) and cobaltate(III) system within presence of some electrolyte were then studied in the following manner.

The violet crystals of cyanocobaltate(II) were prepared filtered, washed briskly with cold 50 % alcohol and dried in the vacuum desiccator. 50.0 c.c. of the electrolyte was taken in the air-tight cell kept in a ice bath(temperature of the solution maintained at 2 @0 3° C) and completed deaeration and displacement of air effected by passing the current of nitrogen for about 25 to 30 minutes 0.30 gm. of the complex was then quickly transferred to the solution in the cell through s(Fig.4.) and the mixture stirred briskly by means of the current of nitrogen. The rate of flow of nitrogen was then slowed down and a slow sweeping current maintained over the solution by raising the inlet tube , throughout the experiment. The potentials of the complex solution were then noted with time, using calomel and a smooth platinum indicator electrode. The surfaceof the electrodes was occasionally brushed by the current of nitrogen in order to keep a clean surface in contact with the solution(This was done gradually because small bubles of hydrogen were found stick upon the surface of the electrode).

A few observations with different electrolytes, are tabulated as follows:- The potentials are recorded with respect to s.c.e. at the temperature of the experiment (2 ±0.5° C)

TABLE CCXXXVIII

Time	Potential in volts w.r. to s.c.c. in presence of				
	KCl(0.5 N)	KCl(2 N.)	$K_2SO_4$0.5N.	K_2SO_4(2 N.)	NH_4Cl(0.5N)
5 mints	0.795	0.791	0.815	0.802	0.785
10 "	0.562	0.539	0.539	0.581	0.573
15 "	0.403	0.378	0.421	0.409	0.339
20 "	0.227	0.214	0.236	0.231	0.183
30 "	0.103	0.095	0.125	0.123	0.058
45 "	0.033	0.078	0.070	0.052	-0.008
60 "	0.004	-0.008	-0.013	-0.021	-0.035
120 "	-0.011	-0.013	-0.021	-0.029	-0.090

Time	NH_4Cl (1 N.)	$(NH_4)_2SO_4$ (0.5 N.)	$(NH_4)_2SO_4$ (2 N.)	KCN (0.1N.)	KCN (0.5 N.)
5 mints	0.703	0.709	0.709	0.[illegible]32	0.[illegible]35
10 "	0.503	0.485	0.463	0.503	0.514
15 "	0.357	0.338	0.303	0.463	0.492
20 "	01176	0.181	0.159	0.274	0.279
30 "	0.043	0.080	0.035	0.158	0.201
45 "	0.093	0.016	0.010	0.096	0.105
60 "	-0.121	-0.028	-0.032	0.037	0.084
120 "	-0.124	-0.032	-0.038	0.032	0.[illegible]

Time	KCl (2N.)	KCl (0.1 N.)	KCl (0.5N.)	KOH (2N.)	(H_2O)
5 mints	0.912	0.906	0.920	0.985	0.840
10 "	0.631	0.628	0.639	0.634	0.591
15 "	0.[illegible]	0.[illegible]	0.[illegible]	0.557	0.[illegible]
20 "	0.[illegible]	0.284	0.[illegible]	0.[illegible]	0.[illegible]
30 "	0.215	0.213	0.250	0.[illegible]	0.149
45 "	0.124	0.120	0.151	0.133	0.031
60 "	0.[illegible]	0.105	0.[illegible]	0.141	0.028
120 "	0.[illegible]	0.101	0.[illegible]	0.[illegible]	0.021

A close examination of table no. ccxxxviii will show that the change in potential of the system is quite rapid in the begining and comes to almost negligible after about an hour when the decomposi-

tion is perhaps almost complete. In no case the potential is found to remain constant which shows that it is impossible to preserve an aquous solution of the complex. In the order of decreasing stabilising influence, the reagents can be arranged as -
KOH , KCN , H_2O , K_2SO_4 , KCl , $(NH_4)_2SO_4$ & NH_4Cl. The higher the concentration of KOH and KCN, the greater their effect on retarding the water oxidation of the complex; but for the salts, after water in the series the higher concentrations have got greater catalytic effect on the decomposition of the complex. In alcohol the complex has been found to be only very sparingly soluble, and aquous alcoholic solutions are equally unstable as aqueous solution. The complex is very readily oxidised in presence of all acids, first to the brown hydroxo-complex and finally to the colourless solution of the hexacyano-cobaltate. .

obtained for reverse titrations (vide curve No. 187 and 188).

The polarographic studies, however, give results of importance which help to understand the controversies connected with its structure. It has been found that freshly prepared complex gives a clear anodic wave with a half wave potential of -0.35 volt (vide curve Nos 189 and 190). This wave is definitely due to pentacyano-cobaltate(ii) since this is suppressed and finally eleiminated by oxiding the complex with hydrogen peroxide. This is contrary to the finding of Hume and Kolthoff (loc.cil) who found that none of the cobaltcyanide complex were oxidised at all.

The oxidised product is irreversibly reduced at the dropping mercury electrode at a potential of -1.28 volts (vide curves 191 and 192). This product is hydroxo-pentacyanocobaltate(iii) as seen by its identity with hydroxo compound prepared by a different method(vide page 280). Both the products give polarograms of the same type with the same half wave potential. Moreover, it can not be hexacyanide as the latter did not give any wave either with KCN or KCl as supporting electrolytes. From these observations it might be concluded that the original product formed by the addition of KCN to cobalt nitrate is $K_3'Co(CN)_5.H_2O'$ which is oxidised in solution to $K_3'Co(CN)_5(OH)'$. Results of similar nature were obtained when the product in the air tight cell obtained after the potentiometric titration was immediately oxidised with a few c.cs of hydrogen peroxide and titrated against 0.1 N HCl (a Beckman P_H meter with glass and calomel electrodes was used). Two distinct breaks in agreement with the observations of Smith and co-werkers(loc. cit), were obtained. Their assumption that the hydroxo- complex undergoes

a change: $2K_3[Co(CN)_5OH] \longrightarrow K_3[Co(CN)_4(OH)_2] + K_3[Co(CN)_6]$ incidentally finds further support by these experiments.

To account for the instability of cobalt(ii)cyanide complex, Pauling[12] suggested that inorder to free two d orbitals for complex formation, the seventh d electron in the cobatl(ii) ion is promoted to a higher energy level where it is easily lost to give the cobalt(iii) complex. This explanation has been criticised on the following grounds. Firstly, because the hydrated cobalt(iii) ion is also diamegnetic, hence like the cyanide, it should have a little tendency to pick up an unshared electron in the excited level and change over to cobalt(ii). But this is contrary to facts. Secondly, Adamson (loc. cit) on the basis of exchange reactions with radio-cyanide has given $K_3'Co(CN)_5'$ as the formula of the complex. This involves a co-ordination number five and a $3d^1\ 4s^1\ 4p^3$ hybridisation and the necessity to free the sixth orbital by promotion of an electron is eliminated. The existence of cobalt cyanide complex with a co-ordination number five is not also theoritically sound. This number is the least likely to exist in a compound with such strongly bound CN groups. Complexes showing this abnormal co-ordination number really differ in the nature of linkages(probably ionic) or have been found to exist as tetraco-ordinated and hexa-co-ordinated ions.[13 to 16,33,34] Amongst these are included IF_5 ; PBr_5; PCl_5; $(CH_3)_3SbCl_2$; Cs_3CoCl_5 etc. Kimball[35] gave trigonal bipyramid, tetragonal pyramid, pentagonal plane and pentagonal pyramid configuration for these compounds. On the basis of Paulings' original theory, a planar configuration is most likely for ions having one d orbital available for bond formation, although Duffey [34] has extended the study of the bi-/pyramidal

structure inorder to calculate the extent to which electrons are involved in the hybridisation . Moreover, compounds in which the central atoms appear to be five co -ordinated in solid state, dissociation takes place in solution. For example Cs_3CoCl_5 has been shown to be made up of tetrahedral tetrachlorocobaltate(ii) ions and Cs^+ and Cl^- ions[36]. Since the complex fails to give any test for free cyanogen ions in solution, the structural proximity to Cs_3CoCl_5 is also not possible.

The magnetic behaviour of the complex is also baffling. The solid has been reported to be diamagnetic[7] while it actually should show paramagnetism. On the other hand, the solution is paramagenetic showing that it contains an unpaired electron. Equally interesting is the behaviour in the case Co^{+++} complexes which show $3d^2\ 4s^1\ 4p^3$ hybridisation and should be diamagnetic. That this is not the case has been demonstrated by Cambi, Ferrari and Nardelli[37] for a number of hexanitro-cobaltate(iii) complexes. The appreciable paramagnetism of these compounds suggests contribution from incompletely quenched orbital magnetism although for the ions of transition elements orbital angular momentum should be negligible and the magnetic moments are only due to electron spin. From the above, itsis thus evident that,magnetic measurements too, fail to give an idea concerning orbital hybridisation, degree of covalent character and probable structure for a large majority of cobalt complexes including, of course, cyanogen complexes.

My experimental results on the physico-chemical investigations on the cobalt(ii) cyanide complex definitely show that five cyanogen radicals are bound to the central atom and further suggest

that the co-ordination number six is maintained by co-ordinating with a water molecule. This behaviour can be explained if we assume that pairing of odd electrons in cobalt(ii) occurs by dimer formation (as in the cobonyl) and the water is not actually co-ordinated but is in the form of lattice water.

Another alternative may be the dimer formation through a water bridge as $(CN)_5Co-\overset{H}{O}-\overset{H}{}Co(CN)_5.H_2O$, the second H_2O being lattice bound. Silver pentacyanoaquocobaltate(iii) complex was, similarly, found to be diamagnetic, but on careful dehydration it gave a compound of the formula $Ag_2'Co(CN)_5'$ which was paramagnetic . This rather goes in favour of a bridge formation as shown above.

It may, therefore, be concluded that cyanocobaltate(ii) exists in a hexa-covalent state both as solid and in solution. In the solid form, the aquopentacyanocobaltate(ii) state is stable in the absence of air and moisture but in solution it is readily converted to the hexa-co-ordinated hydroxopentacyanocobaltate(iii). The latter product again undergoes a change:

$$2K_3[Co(CN)_5OH] \longrightarrow K_3[Co(CN)_4(CN)_2] + K_3[Co(CN)_6].$$

On prolonged standing or on boiling the hexa-cyano-cobaltate(iii) becomes the final product of oxidation. The variations in redox potential of the system $Co(CN)_6^{-4} \rightleftharpoons Co(CN)_6^{-3} + e$ with time may be due to these changes taking place in the aqueous solution. A steady value of the potential is not reached even after a long time and stabilisation could not be achieved in the presence of acids & salts. This behaviour is quite different from that of chromous solutions.

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Résumé.

Amongst the large number of commonly known unstable compounds of the elements of the first transition series, chromous chloride and potassium cyanocaltate(ii) present some very intresting aspects connected with the stabilisation of unstable valence state. A perusal of the literature already cited shows that the problem has not been systematically investigated and certain points not only need further elucidation but altogether a new approach. Chromous chloride solution, inspite of being very unstable, is an important analytical reagent for the estimation of metal ions; and its electrochemical behaviour especially in presence of foreign ions and at some inert electrodes (mercury and platinum), is particularly intresting. Moreover, there is no unanimity of opinion regarding its standard oxidation potential value; and the problem of stabilising chromium(ii) by co-ordination is still in its early stages since very few complexes of Cr(ii) are known and these two are not quite stable. Potassium cyano-cobaltate(ii) is equally unstable and inspite of the fact that it has got a high oxidation potential it cannot be successfully employed as a reducing agent in analytical work. Its structure and electrochemical behaviour, however, present problems of great intrest.

In view of the above, physico-chemical studies on the stability of chromium(ii) and cobalt(ii) were taken up. The problem has been approched from two angles, viz., (i) By investigating the changes in oxidation-reduction potentials of chromous-chromic and cobalto-cobalti-cyanide systems; and

(ii)by preparing an insoluble complex of Cr(ii) ans studying it both in the dried and freshly prepared states. Polarographic studies of cyanocobaltate(ii) were also taken up in order to get an insight into the structural issues related with the complex.

1. Potential of chromous chloride solution in presence of acids, neutral salts, complexing agents, and under controlled p_H.

(a). The solution exibits much greater stability at platinum electrode (about half an hour) than at the mercury electrode (about forty eight hours). The readings obtained were $E_{Hg} = 0.4503$ V and $E_{Pt} = 0.3218$ V for Cr(iii)/Cr(ii), 0.112 the E_o values calculated for this ratio being 0.3948 V and 0.2554 V respectively (vide page 28). Such observations are not to be explained merely on the basis of the catalytic oxidation of the solution at the platinum electrode as given by Forbes and Richter (loc.cit). The factors responsible for such a behaviour may be (i). adsorption of chromous ions at the mercury surface—a fact which finds support in my experiments carried out by stirring the solution at equilibrium when an instantaneous fall in potential was observed (vide table 5, p. 29); and (ii). the role of chloride ions which may be responsible for high potential value and also for a longer period for the attainment of equilibrium, at mercury electrode.

(b). The influence of chloride ions may be seen from the results on the variation in E.M.F. by the addition of HCl and KCl (vide tables 7 and 8, pp. 31 and 32). The values for HCl and KCl were almost the same E_{Hg} (1.5 N HCl) ——0.5113 V;

E_{Hg} (1.5 N KCl) —— 0.5103 for Cr(iii)/Cr(ii) —— 0.112 while at the platinum electrode the values differed very much (E_{Pt} (1.5 N HCl) —— 0.4203 V; E_{Pt}(1.5 N KCl) ——0.3178 for the same chromic-chromous ratio).

(c). The dilution of the solution showed a decrease in potential value (vide table 12, p. 37). This cannot be due to catalytic oxidation ($2CrCl_2 + 2HCl + O = 2CrCl_3 + H_2O$) since the experiments were carried out in a solution not containing HCl, and in an inert atmosphere. The extent to which the chromous and chromic ions undergo hydrolytic dissociation ($Cr^{++} + 2H_2O = Cr(OH)_2 + 2H^+$ and $Cr^{++} + 3H_2O = Cr(OH)_3 + 3H^+$) may influence the chromic-chromous ratio (vide pp. 66 and 74) and hence the potential values.

From the experiments using different electrodes platinum was found to be the most suitable for the potential measurement of chromous-chromic system.

(d). Experimental determination of E_0: very few data exist for the E_0 value of chromous chloride solution obtained by reducing chromic chloride with Zn and HCl . The titration method (vide p. 31 gave E (Pt) for 'neutral' solution = 0.2684 V; and 0.2816 V, 0.3628 V and 0.3682 V in presence of 0.05 N, 1.0 N and 2.0 N HCl respectively. On plotting E_0 values against the concentration of HCl, a parabolic curve was obtained showing that E_0 does not change beyond the acid concentration of 1.8 N (vide curve No. 11). Curves drawn between $\log \frac{Ox}{Red}$ against E gave a slope of 0.057 thereby, showing that the chromous-chromic change is a one electron reaction (vide curve No. 10).

(e). Measurements of E for $CrCl_2$ solution in presence of HCl and

HCl and for $Cr_2(SO_4)_3$ in presence of H_2SO_4 and Na_2SO_4 show that (i) the potential increases with increase in concentration of either HCl or H_2SO_4 , the change being more pronounced with the former and (ii) the chloride ions exert a much greater influence than the sulphate ions (vide tables 19-24, pp. 47-52).

By drawing curves between E and p_H on the one hand, and $p_{Cl'}$ and $p_{SO_4''}$ on the other (vide tables 21-24 and curves 12 to 14) straight lines were obtained and from this the values of E_o and the influence of $H^\cdot$, Cl' and SO_4'' ions have been calculated. Considering the equation

$$E = E_o - 0.059 \log Cr(iii)/Cr(ii) \times (I)^n$$

where I stands for the ion concerned, the values of the constants were determined from the curves (vide p. 68, table no. 27(c)). It was found that there exists a close agreement between the E_o values calculated from the observed potential for different ions and those obtained from the curves. The influence of the various ions on E was found as $Cl' > SO_4'' > H^\cdot$ and the combined influence of $H^\cdot$ and $Cl' > H^\cdot$ and SO_4'', and the following relationships were obtained for the influence of the ions

(1) $E = E_o - 0.059 \log \dfrac{[Cr^{\cdot\cdot\cdot}][Cl']^{0.320}}{[Cr^{\cdot\cdot}]}$

(2) $E = E_o - 0.059 \log \dfrac{[Cr^{\cdot\cdot\cdot}][SO_4'']^{-0.406}}{[Cr^{\cdot\cdot}]}$

(3) $E = E_o - 0.059 \log \dfrac{[Cr^{\cdot\cdot\cdot}][H^\cdot]^{-0.474}}{[Cr^{\cdot\cdot}]}$ (from HCl)

(4) $E = E_o - 0.059 \log \dfrac{[Cr^{\cdot\cdot\cdot}][H^\cdot]^{-0.121}}{[Cr^{\cdot\cdot}]}$ (from H_2SO_4)

Experimental results regarding the influence of chloride and sulphate ions may be explained by assuming that the following

reactions take place in solution.

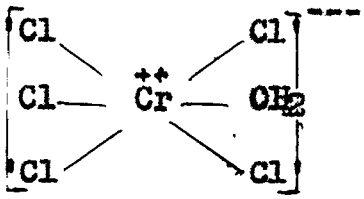
$$CrCl_2 + xKCl = K_xCrCl_{2+x} \text{ ————— (1)}$$

$$CrCl_3 + yKCl = K_yCrCl_{3+y} \text{ ————— (ii)}$$

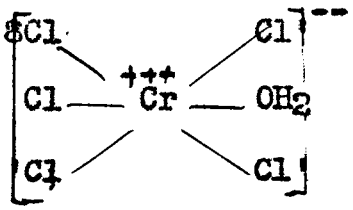
$$2CrSO_4 + xNa_2SO_4 = Na_{2x}Cr_2(SO_4)_{2+x} \text{ ————— (iii)}$$

$$\text{and } Cr_2(SO_4)_3 + yNa_2SO_4 = Na_{2y}Cr_2(SO_4)_{3+y} \text{ ————— (iv)}$$

From the values of E and the constants determined from the curve, the ratio x:y for KCl was found as 3:2 and for Na_2SO_4 as 6:5 (vide pp-69-73). The complex anions formed can be represented as:

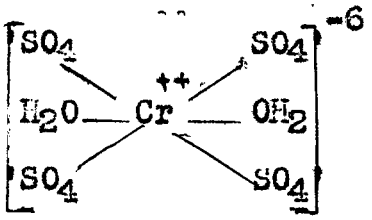


E.A.N. = 22+ 12 = 34.

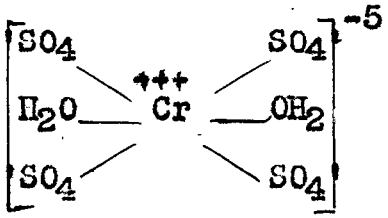


E.A.N. = 21 + 12 = 33.

and



E.A.N. = 22 +12 = 34



E.A.N. = 21 + 12 = 33.

These complexes existing in solution show that strong covalent bonding between the central atoms and the co-ordinating ions does not probably exist. These formulae further show that the oxidation state of the anions are due to one electron transfer.

The influence of hydrogen ions on the potential of the system appears to be entirely different from that of the anions and considering the values of n (stable no 27(c) p. 68) it can be seen that such relationship as:

$$E_1 = E_o - 0.059 \log \frac{[Cr^{\cdot\cdot\cdot}][H^{\cdot}]^{n_1}[Cr^{'}]^{n_2}}{[Cr^{\cdot\cdot}]}$$

$$\text{and } E \leq E_o - 0.059 \log \frac{[Cr^{\cdot\cdot\cdot}][H^{\cdot}]^{n_3}[SO^{''}]^{n_4}}{[Cr^{\cdot\cdot}]}$$

cannot hold good. The role of hydrogen ions is also not to influence the hydrolysis of $CrCl_2$ and $CrCl_3$ according to the simple mechanism,

$$CrCl_2 + 2H_2O \rightleftharpoons Cr(OH)_2 + 2HCl$$

$$\text{and } CrCl_3 + 3H_2O \rightleftharpoons Cr(OH)_3 + 3HCl$$

since it would mean higher potential values for low hydrogen ion concentration. The abnormal behaviour in highly acidic solutions may be attributed to the existence of different isomeric forms of Cr(iii), their hydrolysability and the difference in the stability of Cr(ii) and Cr(iii) hydroxides(vide p. 74). However, insolutions of low acidity (obtained by adding gradually increasing amounts of NaOH) an increase in potential with decrease in ($H^{\cdot}$), i.e. with increase in p_H, is observed. This takes place beyond a p_H of 3.15 (vide curve no. 15). It is highly probable that in this range, the reactions $Cr(OH)_2 \rightleftharpoons Cr^{\cdot\cdot} + 2OH^{'}$ and $Cr(OH)_3 \rightleftharpoons Cr^{\cdot\cdot\cdot} + 3OH^{'}$ take place and on the basis of the difference in K(1×10^{-17} and 6.7×10^{-31}) for $Cr^{\cdot\cdot}$ and $Cr^{\cdot\cdot\cdot}$ hydroxides, these results have been explained (vide p. 75).

(f). The potential values in presence of salts and complexing agents, such as oxalic, tartaric and citric acids and their salts; phosphates molybdates, pyridine etc. fall under two catagories: (i) a low p_H range of 1.46 to 6.36 and (ii) a high p_H range of 7.54 to 10.4. In the former high potential values

are obtained when either complexing anions, or sufficient hydrogen ions to check the hydrolytic tendencies of chromium ions, are present while low values are obtained in presence of acids and salts which form complexes with a very stable ligand (oxalic, citric and tartaric acids and their salts etc). In the latter case high potential values are obtained with NH_4OH and pyridine. The case is similar to that observed by the addition of NaOH (vide pp. 75, 76).

2. Use of chromous chloride as an analytical reagent.

Titrations were carried out between copper sulphate and chromous chloride in presence of acids (hydrochloric, sulphuric and acetic acids) and their salts at 25° and 55° . It was found that the second break (reduction to metallic copper) is pronounced in the majority of cases, sharp break in the first stage ($Cu^{\cdot\cdot} \longrightarrow Cu^{\cdot} - \ominus$) being observed in presence of HCl, KCl or a mixture of both. With sulphuric acid the second break was fairly sharp but with Na_2SO_4 or a mixture of Na_2SO_4 and H_2SO_4 , typical titration curves could not be obtained (vide curve nos.17-61, pp. 83- 103). The presence ofacids help in the attainment of equilibrium at the electrodes quickly and, in this way, their presence is desirable; otherwise the chloride ions (either from HCl, KCl or NH_4Cl) are enough to give good breaks. The concentration of chromous chloride determined by these titrations gave values coinciding with those obtained by other methods only from the second break for lower concentrations of HCl or KCl or both and from the first break for higher concs.

Values lower than the actual concentration of chromous chloride (0.2739 M.) were obtained on carrying out the titrations at a higher temperature(table nos. 63-77, pp. 107-115). from a large number of titrations it has been concluded that the conditions laid down by Zintl and Rûenacker (loc. cit) for such titrations need modification . Neither excess of chloride ions is undesirable nor it is necessary to carry out titrations at 90° to obtain good results. On the contrary excess of chloride ions help in realising the first break. The results have been discussed (vide pp. 116-120) and they give support to the view point put forward in explaining the role of chromous-chromic system.

3. The polarographic studies of $Cr^{...}$ and $Cr^{..}$ ions.

Although the polarographic studies were carried out to investigate the abnormal variations in the potential on adding different varieties of chromic chloride to chromous chloride solution, the results failed to through light on this phenomenon . But confirmation to what has already been seen about the behaviour of chromous-chromic system could be obtained on the basis of different varieties of chromic chloride at the dropping mercury electrode, and anodic wave of chromium(ii).

Four samples, freshly prepared and aged solutions of green hydrate, violet solution and Cr(iii) obtained by the oxidation of chromous chloride were reduced at the dropping mercury electrode using different concentrations of supporting electrolyte (KCl). Two stages of reduction were observed; the E/2 value for the second wave was the same for all samples, being independent of either the concentration of Cr(iii) or KCl(vide curve Nos. 78-102, pp.129-138). The E/2 values for the different samples

were: (i) 1.1 volts for Cr(iii) obtained from Cr(ii); (ii)0.8 volt for freshly prepared green hydrate; (iii) 0.95 volt for the aged green variety and (iv) 1.0 volt for the violet. It appears that the violet variety is the most stable and that Cr(ii) gives high value due to the probable formation of $CrCl_2$ —O—$CrCl_2$.

Anodic waves of Cr(ii) obtained by the reduction of the green hydrate (by Zn and HCl) were studied in presence of HCl, H_2SO_4 and HAc and their salts, and complexing agents like oxalate, tartarate, citrate etc. Variations in Cr(iii)/Cr(ii) did not influence either the anodic or cathodic half wave potentials. Different supporting electrolytes influenced the anodic potentials to different extents. Oxidation could not be observed in presence of citrate, tartarate and oxalate. From the observations (vide curve nos. 141-144 p. 172) it was concluded that the presence of H or Cl ions or both are essential for better utilisation of chromous chloride as a reducing agents

4. Stabilisation of Cr(ii) by interaction with potassium ferrocyanide.

Although Cr(iii) does not give precipitate with potassium ferrocyanide at ordinary temperature, Cr(ii) gives precipitates ranging from dirty yellow to dirty green with this reagent. Precipitation was carried out under the following conditions(i) Chromous chloride added to excess of potassium ferrocyanide(ii) Potassium ferrocyanide added to excess of chromous chloride and(iii) mixing the reactants as to give a precipitate containg neither of them in excess. The dried precipitate gave six moles of bound water per mole of the complex. The formulae of the three samples were

found to be $K_2CrFeCy_6$; Cr_2FeCy_6 and $K_2Cr_3(FeCy_6)_2$ respectively (vide pp. 197-199).

Conductometric and potentiometric titrations (direct and reverse) between chromous chloride and potassium ferrocyanide of different concentrations carried out in aquous and aquous- alcoholic media, confirm the results of analysis. The composition of the complexes were found to be $K_2CrFeCy_6$ and Cr_2FeCy_6. The difference between the theoretical and the observed titre values (vide tables 185, 186 and 199; pp. 217, 218 and 231) point towards the adsorption capacities of the precipitates. Titre values approach the theoretical inpresence of alcohol. It may be due to the suppression of adsorption or hydrolysis or both due to the presence of alcohol.

Amperometric titrations between chromous chloride and potassium ferrocyanide were carried out to confirm the above results on the composition of the complex. Direct and reverse titrations were carried out at a potential of -0.2 volt. and unlike conductometry and potentiometry, only one break could be obtained (vide curve nos. 178to 183) pointing towards the formation of Cr_2FeCy_6. Discrepencies in the titre values in aquous medium could again be attributed to the adsorptive behaviour of the complex. Results approaching the theoretical values were obtained in aquous alcoholic media (vide table 208-209; page 242).

The different methods used for finding out the composition of chromous ferrocyanide, besides giving the formulae of the different complexes formed at various stages of titration under different conditions, also give a fairly good idea of the comparative marits and demerits of these methods. It is rather surprising

to find that the more recent technique, that is, amperometry fails to show the existence of the complex $K_2CrFeCy_6$. On the other hand conductometry and potentiometry not only give titre values which show the existence of $K_2CrFeCy_6$ but also of $Cr_4[FeCy_6]_3$. It is thus evident that the latter methods have not outlived their utility in elucidating the composition of insluble complexes.

The possibility of the existence of super complexes for chromous ferrocyanide has been envisaged. Thus the complexes should be represented as (i) $K_2[Cr(FeCy_6)]$ and (ii) $Cr[Cr(FeCy_6)]$. Theoretical considerations support such structures although X-Ray and magnetic data are not available (vide pp. 261-262). Unlike Fe^{++} and V^{++} chromous ions are not stabilised by the cyanide ions as can be seen from the potential of $[Cr(CN)_6]^{-4}$ to $[Cr(CN)_6]^{-3}$ (-) (1.284 volt). But this purpose is very well served by nuclear polymerisation with ferrocyanogen ions.

Quantitative study of the adsorption of ferrocyanogen and chromous ions on the freshly precipitated complex both in aqueous and aqueous-alcoholic media was carried out with a view to confirm the results on the composition of the complex. The maximum adsorption of ferrocyanide as obtained from curves (A, B; P. 249) was found to be nearly one mole per mole of the complex in aqueous medium and 0.098 mole in aqueous-alcoholic medium. Chromous ions were adsorbed to a much lesser extent, the values being 0.3 and 0.1 mole per mole of the complex respectively(vide curve C, D; page 238). Typical adsorption isotherms were obtained in each case. Evidence for the formation of adsorption complex with the formula Cr_2FeCy_6. K_4FeCy_6 is forthcoming(vide p. 237).

Hydrolysis of the complex was found to be negligible at ordinary temperature, but at 55° a suspension of 1 gm. of the complex in 100 c.c. water was about 1 %. Further dilution (4 times) increased the value to 1.8 % (vide page 283). The hydrolysis of the complex may be represented by the following reactions:

$$Cr_2FeCy_3 + 2H_2O \rightleftharpoons H_2CrFeCy_3 + Cr(OH)_2$$

and $$H_2CrFeCy_6 + 2H_2O \rightleftharpoons H_4FeCy_3 + Cr(OH)_2$$

and this is also justified on assuming the existence of poly-nuclear complex anion $[CrFeCy_6]^{---}$

5. Potassium cyanocobaltate(ii).

In part II attempt has been made to find an answer to the contradictions regarding the structure of potassium cyano-cobaltate(ii). Preliminary experiments on the potential variations in the system $Co(CN)_6^{----} \rightleftharpoons Co(CN)_6^{---} + \ominus$ are also described.

The complex prepared by the interaction of Co(ii) with potassium cyanide, give on analysis, a compound with the formula $K_3Co(CN)_5.H_2O$ with about 0.1 N KCN adsorbed per mole (vide p. 273). Potentiometric and amperometric titrations carried out between $Co(NO_3)_2$ and KCN also give support to the formation of a pentacyano-cobaltate(vide pp. 276, 277, 283-285 and curves 185-188, 195-198).

Polarographic studies, however, also help to some extent in deciding whether the complex is hexa or penta co-ordinated. The freshly prepared complex gives anodic wave with a half wave potential of -0.43 volts (vide curves 189 and 190)

This is due to pentacyano-cobaltate(ii) since it is suppressed and finally eliminated by a oxidising with H_2O_2. The oxidised product was then irreversibly reduced at the dropping mercury electrode at a potential of -1.28 volts (vide curves 191-192). The product was the same as the hydroxo-pentacyano-cobaltate(iii) prepared separately, since both the products gave polarograms with same half wave potentials (vide p. 290). From these experiments the conclusion arrived at is that the complex has got the formula $K_3\{Co(CN)_5.H_2O\}$ and it is oxidised to $K_3\{Co(CN)_5(OH)\}$. Theoretical considerations in support of the formula have been given (vide pp. 290 and 291).

From the experimental results, it can be safely concluded that five cyanogen radicals are bound to the central atom and that a co-ordination number of six is maintained by co-ordinating with a water molecule. The other alternative may be the formation of a dimer through a water bridge.

$$(CN)_5Co—\overset{H}{\underset{H}{O}}—Co(CN)_5.H_2O$$ (vide page 293).

Potential studies show that a steady value at the platinum electrode is not reached even after a long time and that stabilisation is not achieved in the presence of acids, bases and salts.

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